Preface

Welcome to *Chemistry*, an OpenStax resource. This textbook was written to increase student access to high-quality learning materials, maintaining highest standards of academic rigor at little to no cost.

About OpenStax

OpenStax is a nonprofit based at Rice University, and it's our mission to improve student access to education. Our first openly licensed college textbook was published in 2012, and our library has since scaled to over 25 books for college and AP® courses used by hundreds of thousands of students. OpenStax Tutor, our low-cost personalized learning tool, is being used in college courses throughout the country. Through our partnerships with philanthropic foundations and our alliance with other educational resource organizations, OpenStax is breaking down the most common barriers to learning and empowering students and instructors to succeed.

About OpenStax's resources

Customization

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Errata

All OpenStax textbooks undergo a rigorous review process. However, like any professional-grade textbook, errors sometimes occur. Since our books are web based, we can make updates periodically when deemed pedagogically necessary. If you have a correction to suggest, submit it through the link on your book page on OpenStax.org. Subject matter experts review all errata suggestions. OpenStax is committed to remaining transparent about all updates, so you will also find a list of past errata changes on your book page on OpenStax.org.

Format

You can access this textbook for free in web view or PDF through OpenStax.org, and in low-cost print and iBooks editions.

About *Chemistry*

Chemistry is designed to meet the scope and sequence requirements of the two-semester general chemistry course. The textbook provides an important opportunity for students to learn the core concepts of chemistry and understand how those concepts apply to their lives and the world around them. The book also includes a number of innovative features, including interactive exercises and real-world applications, designed to enhance student learning.

Coverage and scope

Our *Chemistry* textbook adheres to the scope and sequence of most general chemistry courses nationwide. We strive to make chemistry, as a discipline, interesting and accessible to students. With this objective in mind, the content of this textbook has been developed and arranged to provide a logical progression from fundamental to more advanced concepts of chemical science. Topics are introduced within the context of familiar experiences whenever possible, treated with an appropriate rigor to satisfy the intellect of the learner, and reinforced in subsequent discussions of related content. The organization and pedagogical features were developed and vetted with feedback from chemistry educators dedicated to the project.

Pedagogical foundation and features

Throughout *Chemistry*, you will find features that draw the students into scientific inquiry by taking selected topics a step further. Students and educators alike will appreciate discussions in these feature boxes.

> **Chemistry in Everyday Life** ties chemistry concepts to everyday issues and real-world applications of science that students encounter in their lives. Topics include cell phones, solar thermal energy power plants, plastics recycling, and measuring blood pressure.
> **How Sciences Interconnect** feature boxes discuss chemistry in context of its interconnectedness with other scientific disciplines. Topics include neurotransmitters, greenhouse gases and climate change, and proteins and enzymes.
> **Portrait of a Chemist** presents a short bio and an introduction to the work of prominent figures from history and present day so that students can see the "face" of contributors in this field as well as science in action.

Comprehensive art program

Our art program is designed to enhance students' understanding of concepts through clear, effective illustrations, diagrams, and photographs.

(a) (b) (c) (d) (e)

Beam of α particles

Radium source of α particles

A very small number of α particles are significantly deflected

A few α particles are slightly deflected

Most α particles pass straight through foil

Luminescent screen to detect scattered α particles

Thin gold foil

HCl(g)

H₂O(l)

$HCl(g) \longrightarrow HCl(aq)$

(a)

Cl⁻(aq)

H₂O(l)

H₃O⁺(aq)

$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

(b)

$3d_{xy}$

$3d_{xz}$

$3d_{yz}$

$3d_{z^2}$

$3d_{x^2-y^2}$
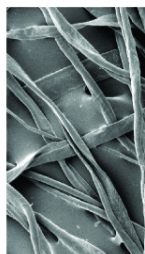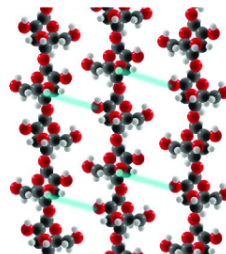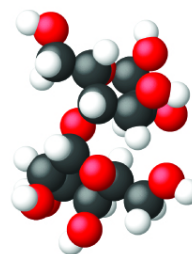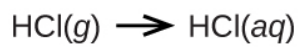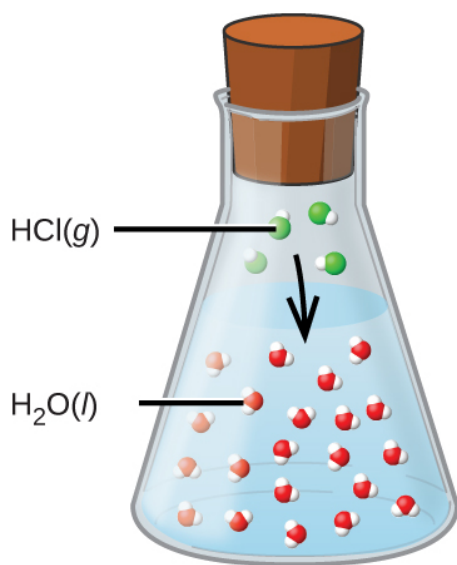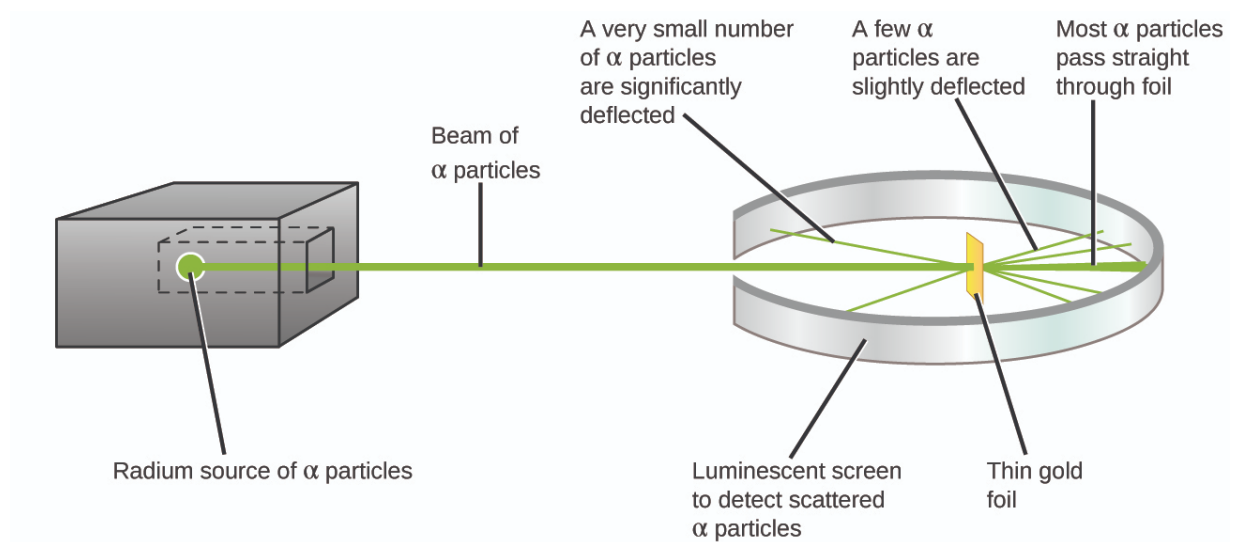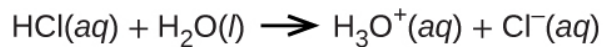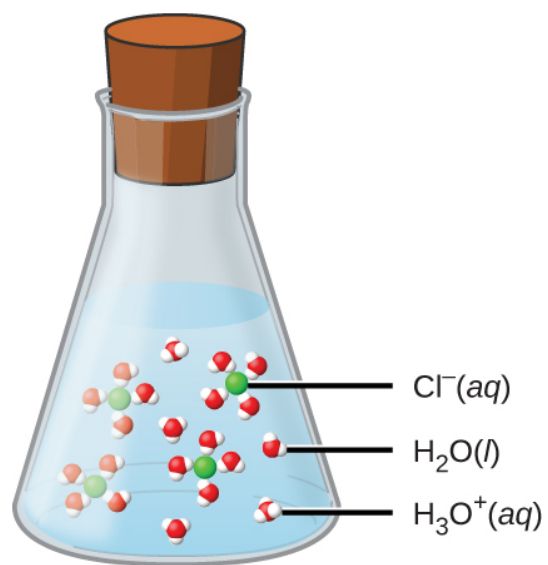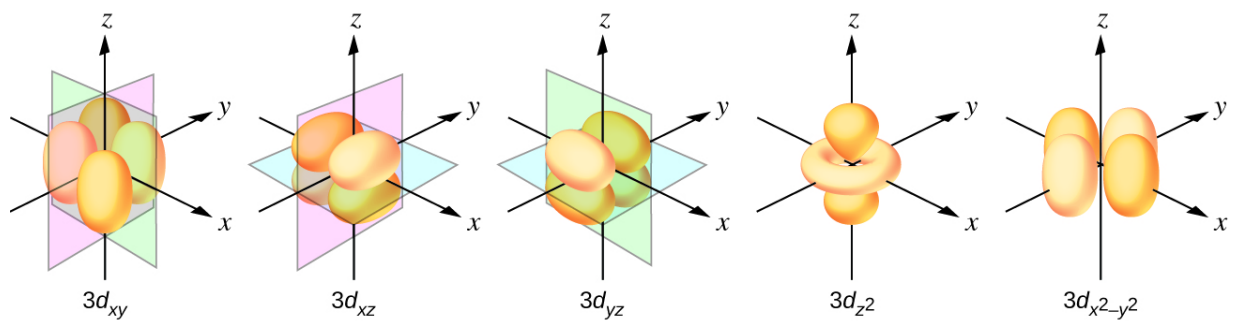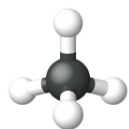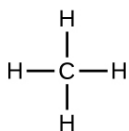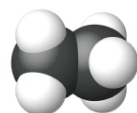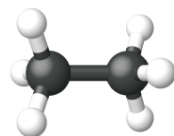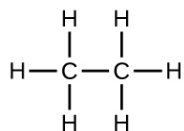
methane
CH_4

ethane
CH_3CH_3 or C_2H_6
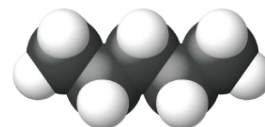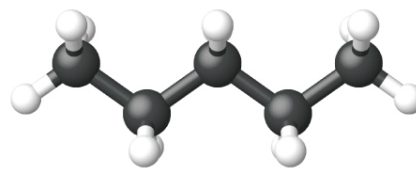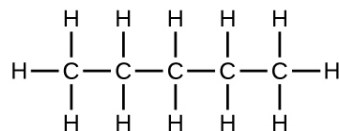
pentane
$CH_3CH_2CH_2CH_2CH_3$ or C_5H_{12}
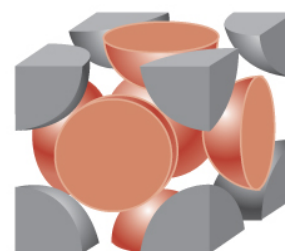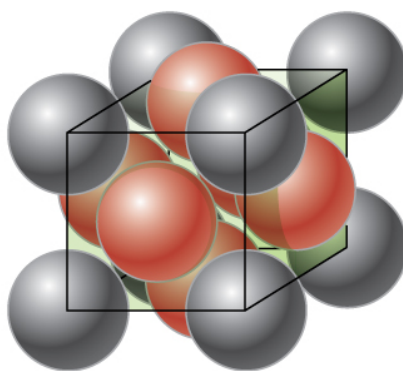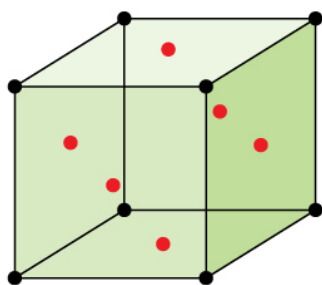
Face-centered cubic structure
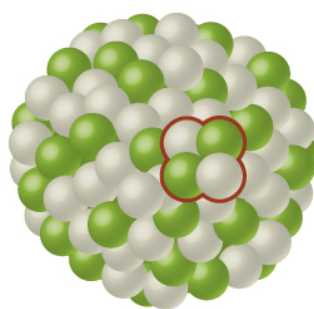
Parent nucleus
uranium-238
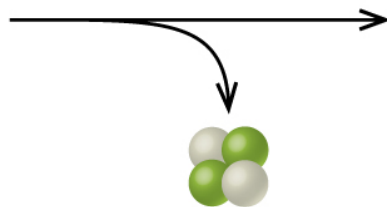
α particle
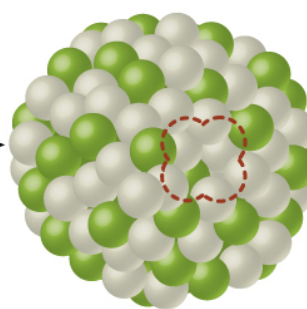
Daughter nucleus
thorium-234

Interactives that engage

Chemistry incorporates links to relevant interactive exercises and animations that help bring topics to life through our **Link to Learning** feature. Examples include:

> PhET simulations
> IUPAC data and interactives
> TED Talks

Assessments that reinforce key concepts

In-chapter **Examples** walk students through problems by posing a question, stepping out a solution, and then asking students to practice the skill with a "Check Your Learning" component. The book also includes assessments at the end of each chapter so students can apply what they've learned through practice problems.

Additional resources

Student and instructor resources

We've compiled additional resources for both students and instructors, including Getting Started Guides, an instructor solutions manual, and PowerPoint slides. Instructor resources require a verified instructor account, which you can apply for when you log in or create your account on OpenStax.org. Take advantage of these resources to supplement your OpenStax book.

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resources to use in their own courses, including additional ancillaries, teaching material, multimedia, and relevant course content. We encourage instructors to join the hubs for the subjects most relevant to your teaching and research as an opportunity both to enrich your courses and to engage with other faculty.

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# Introduction
class="introduction"

- Chemistry in Context
- Phases and Classification of Matter
- Physical and Chemical Properties
- Measurements
- Measurement Uncertainty, Accuracy, and Precision
- Mathematical Treatment of Measurement Results
- Module for Testing Functions of Various Items to See How They Generate in the PDF

Chemical substances and processes are essential for our existence, providing sustenance, keeping us clean and healthy, fabricating electronic devices, enabling transportation, and much more. (credit "left": modification of work by "vxla"/Flickr; credit "left middle": modification of work by "the Italian voice"/Flickr;

Your alarm goes off and, after hitting "snooze" once or twice, you pry yourself out of bed. You make a cup of coffee to help you get going, and then you shower, get dressed, eat breakfast, and check your phone for messages. On your way to school, you stop to fill your car's gas tank, almost making you late for the first day of chemistry class. As you find a seat in the classroom, you read the question projected on the screen: "Welcome to class! Why should we study chemistry?"

Do you have an answer? You may be studying chemistry because it fulfills an academic requirement, but if you consider your daily activities, you might find chemistry interesting for other reasons. Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use—like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car—all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this course, you

will learn many of the essential principles underlying the chemistry of modern-day life.

Chemistry in Context
By the end of this module, you will be able to:

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavors involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well—clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans began to practice chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. Subsequently, they began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants. Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were combined to form alloys—for example, copper and tin were mixed together to make bronze—and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation.

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations were spread from Egypt, China, and the eastern Mediterranean by alchemists, who endeavored to transform "base metals"

such as lead into "noble metals" like gold, and to create elixirs to cure disease and extend life ([link]).

This portrayal shows an alchemist's workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Chemical Heritage Foundation)

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter. This effort has been so successful that many people do not realize either the central position of chemistry among the sciences or the importance and universality of chemistry in daily life.

Chemistry: The Central Science

Chemistry is sometimes referred to as "the central science" due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields ([link]). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world's population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.
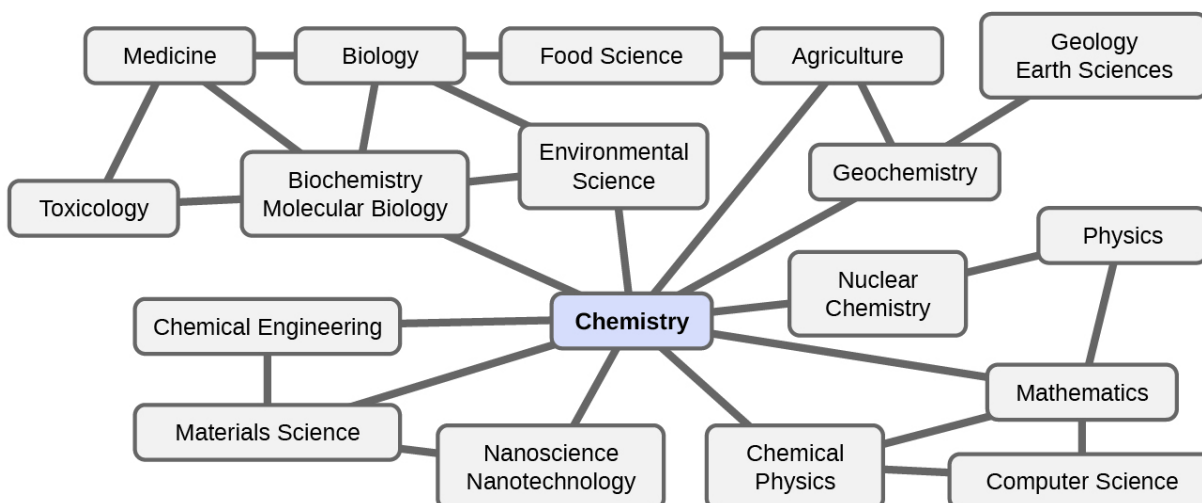
Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

What are some changes in matter that are essential to daily life? Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this course, you will discover many different examples of changes in the composition and structure of matter, how to classify these changes and how they occurred, their causes, the changes in energy that accompany them, and the principles and laws involved. As you learn about these things, you will be learning **chemistry**, the study of the composition, properties, and interactions of matter. The practice of chemistry is not limited to chemistry books or laboratories: It happens whenever someone is involved in changes in matter or in conditions that may lead to such changes.

The Scientific Method

Chemistry is a science based on observation and experimentation. Doing chemistry involves attempting to answer questions and explain observations in terms of the laws and theories of chemistry, using procedures that are

accepted by the scientific community. There is no single route to answering a question or explaining an observation, but there is an aspect common to every approach: Each uses knowledge based on experiments that can be reproduced to verify the results. Some routes involve a **hypothesis**, a tentative explanation of observations that acts as a guide for gathering and checking information. We test a hypothesis by experimentation, calculation, and/or comparison with the experiments of others and then refine it as needed.

Some hypotheses are attempts to explain the behavior that is summarized in laws. The **laws** of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of explaining a large body of experimental data, it can reach the status of a theory. Scientific **theories** are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory explanations, but they can be modified if new data become available. The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the **scientific method** ([link]).
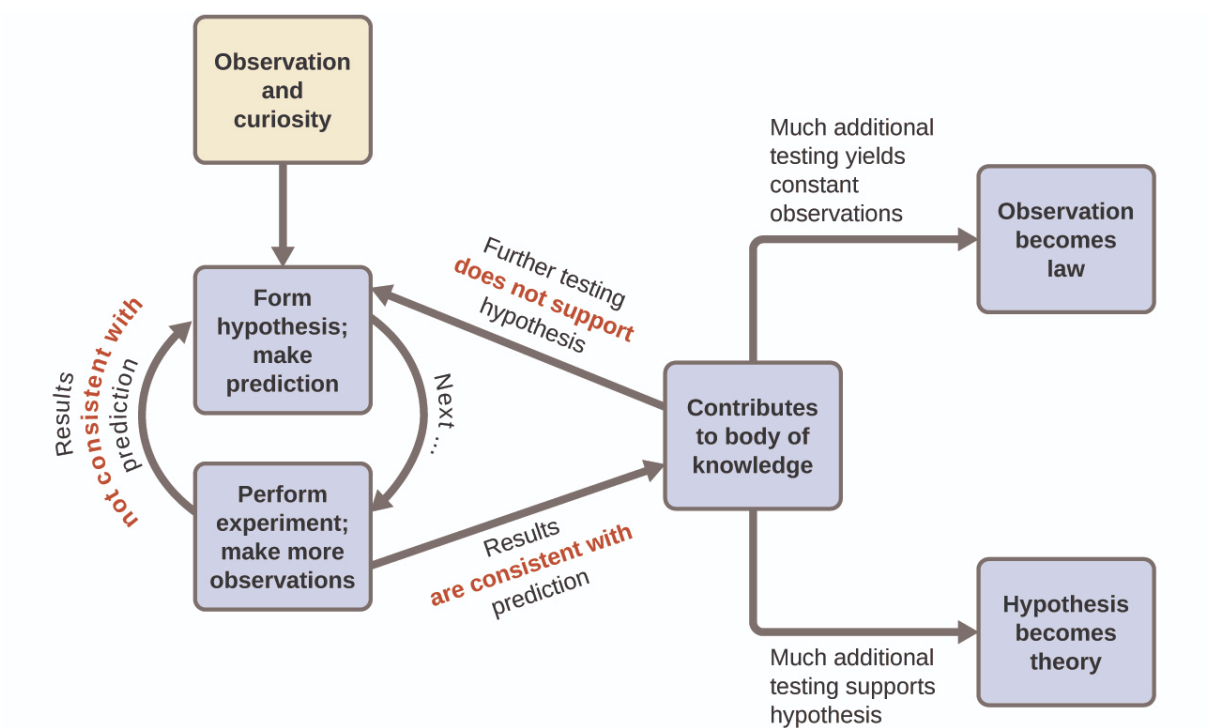
The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of considering and describing chemical behavior.

Macro is a Greek word that means "large." The **macroscopic domain** is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain includes everyday and laboratory chemistry, where we observe and measure

physical and chemical properties, or changes such as density, solubility, and flammability.

The **microscopic domain** of chemistry is almost always visited in the imagination. *Micro* also comes from Greek and means "small." Some aspects of the microscopic domains are visible through a microscope, such as a magnified image of graphite or bacteria. Viruses, for instance, are too small to be seen with the naked eye, but when we're suffering from a cold, we're reminded of how real they are.

However, most of the subjects in the microscopic domain of chemistry—such as atoms and molecules—are too small to be seen even with standard microscopes and often must be pictured in the mind. Other components of the microscopic domain include ions and electrons, protons and neutrons, and chemical bonds, each of which is far too small to see. This domain includes the individual metal atoms in a wire, the ions that compose a salt crystal, the changes in individual molecules that result in a color change, the conversion of nutrient molecules into tissue and energy, and the evolution of heat as bonds that hold atoms together are created.

The **symbolic domain** contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs and drawings. We can also consider calculations as part of the symbolic domain. These symbols play an important role in chemistry because they help interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that makes chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures, will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures ([link]) are macroscopic observations. But some properties of water fall into the microscopic domain—what we

cannot observe with the naked eye. The description of water as comprised of two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (*g*) for gas, (*s*) for solid, and (*l*) for liquid are also symbolic.
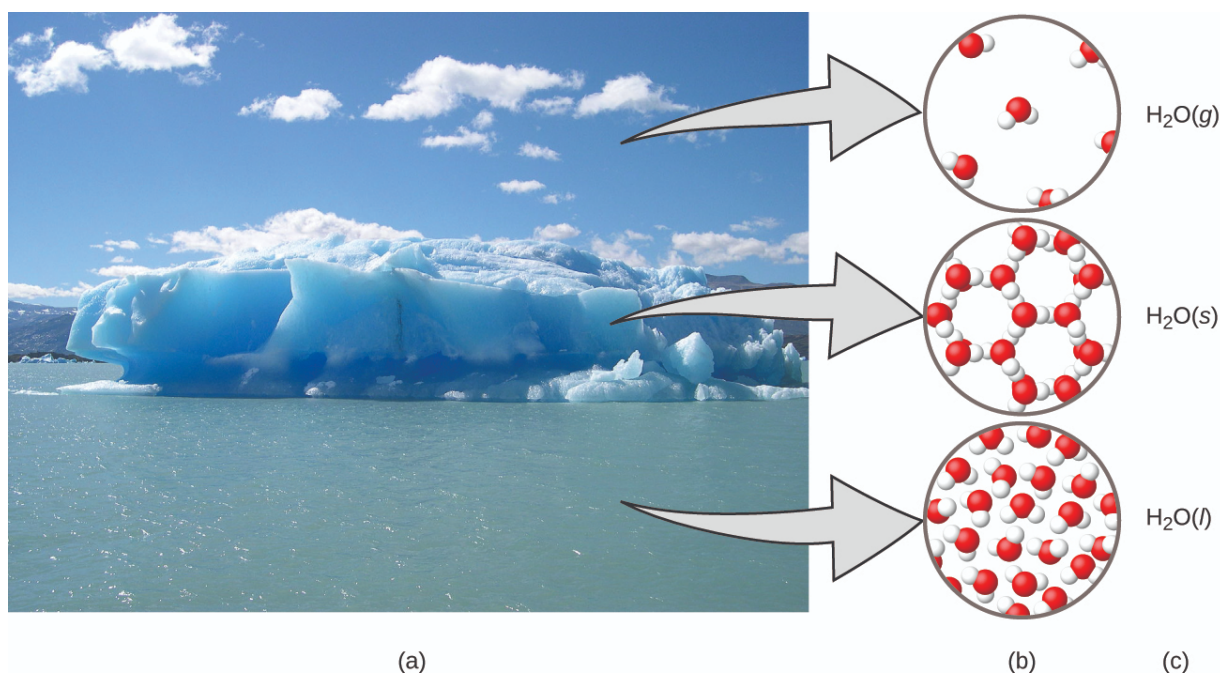
(a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (*g*), (*s*), and (*l*) symbolize its phases. Note that clouds are actually comprised of either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity. (credit a: modification of work by "Gorkaazk"/Wikimedia Commons)

Key Concepts and Summary

Chemistry deals with the composition, structure, and properties of matter, and the ways by which various forms of matter may be interconverted. Thus, it occupies a central place in the study and practice of science and technology. Chemists use the scientific method to perform experiments, pose hypotheses, and formulate laws and develop theories, so that they can better understand the behavior of the natural world. To do so, they operate in the macroscopic, microscopic, and symbolic domains. Chemists measure, analyze, purify, and synthesize a wide variety of substances that are important to our lives.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.

Solution:

Place a glass of water outside. It will freeze if the temperature is below 0 °C.

Exercise:

Problem:

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

(a) Falling barometric pressure precedes the onset of bad weather.

(b) All life on earth has evolved from a common, primitive organism through the process of natural selection.

(c) My truck's gas mileage has dropped significantly, probably because it's due for a tune-up.

Exercise:

Problem:

Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

(a) The pressure of a sample of gas is directly proportional to the temperature of the gas.

(b) Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.

(c) At a higher temperature, solids (such as salt or sugar) will dissolve better in water.

Solution:

(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation)

Exercise:

Problem:

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

(a) The mass of a lead pipe is 14 lb.

(b) The mass of a certain chlorine atom is 35 amu.

Exercise:

Problem:

Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For those in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.

(a) A certain molecule contains one <u>H</u> atom and one Cl atom.

(b) <u>Copper wire</u> has a density of about 8 g/cm^3.

(c) The bottle contains 15 grams of <u>Ni powder</u>.

(d) A <u>sulfur molecule</u> is composed of eight sulfur atoms.

Solution:

(a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic

Exercise:

Problem:

According to one theory, the pressure of a gas increases as its volume decreases because the molecules in the gas have to move a shorter distance to hit the walls of the container. Does this theory follow a macroscopic or microscopic description of chemical behavior? Explain your answer.

Exercise:

Problem:

The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behavior? Explain your answer.

Solution:

Macroscopic. The heat required is determined from macroscopic properties.

Glossary

chemistry
    study of the composition, properties, and interactions of matter

hypothesis
    tentative explanation of observations that acts as a guide for gathering and checking information

law
    statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

macroscopic domain
    realm of everyday things that are large enough to sense directly by human sight and touch

microscopic domain
    realm of things that are much too small to be sensed directly

scientific method
    path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory

symbolic domain
    specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

theory
    well-substantiated, comprehensive, testable explanation of a particular aspect of nature

Phases and Classification of Matter
By the end of this section, you will be able to:

- Describe the basic properties of each physical state of matter: solid, liquid, and gas
- Define and give examples of atoms and molecules
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition
- Distinguish between mass and weight
- Apply the law of conservation of matter

Matter is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth ([link]). A **solid** is rigid and possesses a definite shape. A **liquid** flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A **gas** takes both the shape and volume of its container.

Solid	Liquid	Gas
Has fixed shape and volume	Takes shape of container Forms horizontal surface Has fixed volume	Expands to fill container
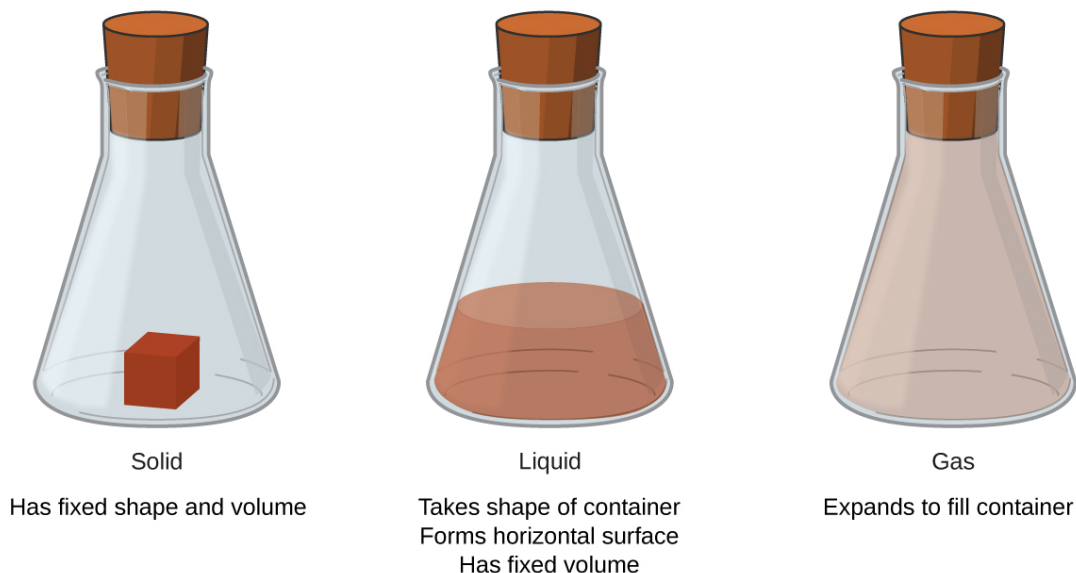
The three most common states or phases of matter are solid, liquid, and gas.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A **plasma** is a gaseous state of matter that contains appreciable numbers of electrically charged particles ([link]). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars,

plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.

A plasma torch can be used to cut metal. (credit: "Hypertherm"/Wikimedia Commons)

Note:

In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The **mass** of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. **Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon's gravity is only one-sixth that of the earth's. She may feel "weightless" during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never "massless."

The **law of conservation of matter** summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter ([link]). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.
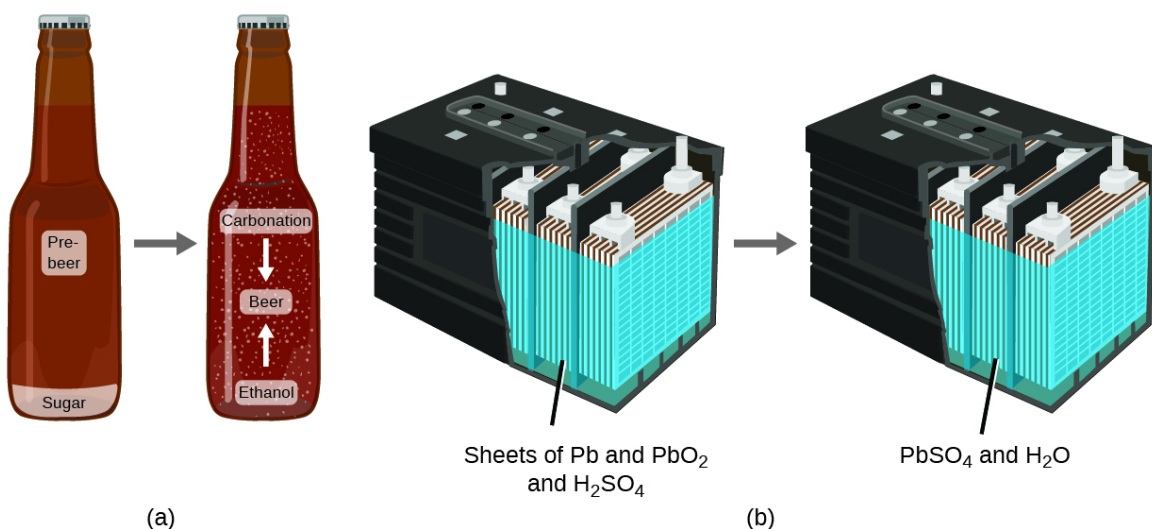
(a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

Atoms and Molecules

An **atom** is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning "indivisible") ([link]). This atom would no longer be gold if it were divided any further.
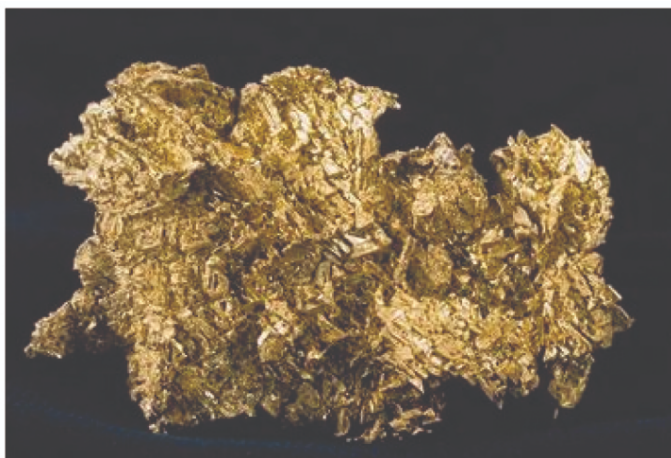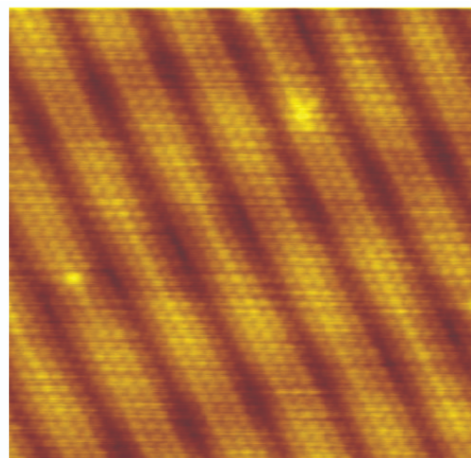
(a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by "Erwinrossen"/Wikimedia Commons)

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry. Other aspects of Dalton's atomic theory are still used but with minor revisions (details of Dalton's theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom "dimes" to cover it. ([link]) shows increasingly close microscopic and atomic-level views of ordinary cotton.
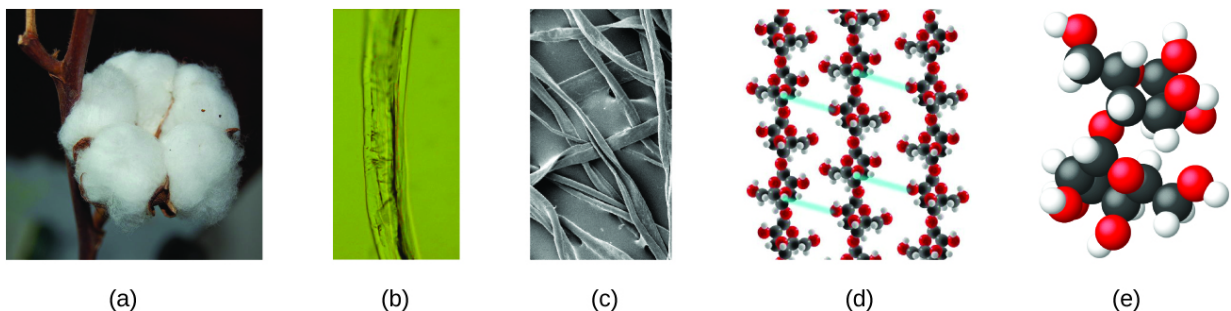
These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by "Featheredtar"/Wikimedia Commons)

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about 3×10^{-13} grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or 3×10^{14}) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms ([link]). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A **molecule** consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.
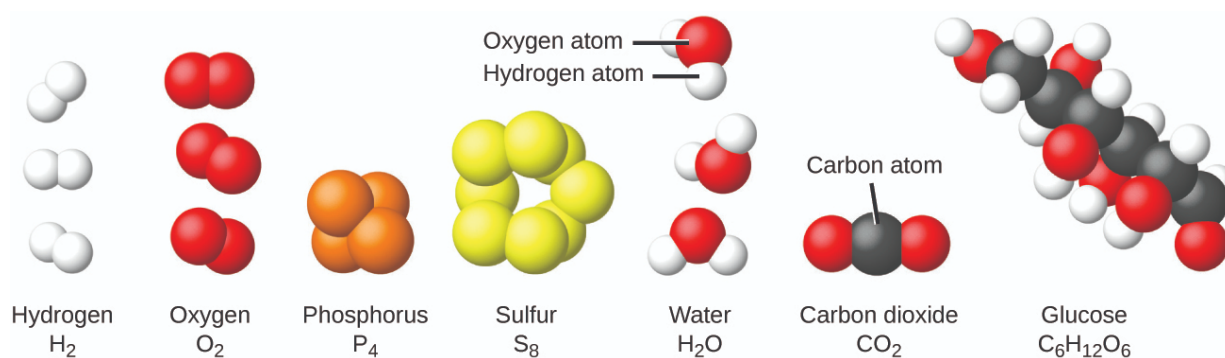
The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

Classifying Matter

We can classify matter into several categories. Two broad categories are mixtures and pure substances. A **pure substance** has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called **elements**. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called **compounds**. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen ([link]). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).
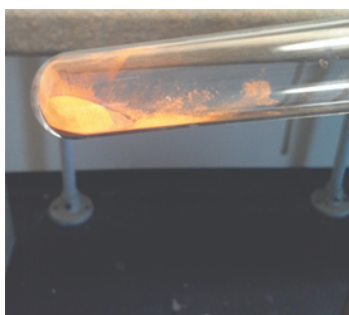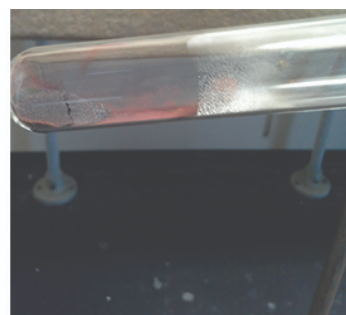
(a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

Note:

Many compounds break down when heated. This site shows the breakdown of mercury oxide, HgO. You can also view an example of the photochemical decomposition of silver chloride (AgCl), the basis of early photography.

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A **mixture** is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a **heterogeneous mixture**. Italian dressing is an example of a heterogeneous mixture ([link]).

Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A **homogeneous mixture**, also called a **solution**, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly ([link]). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.

(a)   (b)

(a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a "left": modification of work by John Mayer; credit a "right": modification of work by Umberto Salvagnin; credit b "left: modification of work by Jeff Bedford)

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties by which we can distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in ([link]).
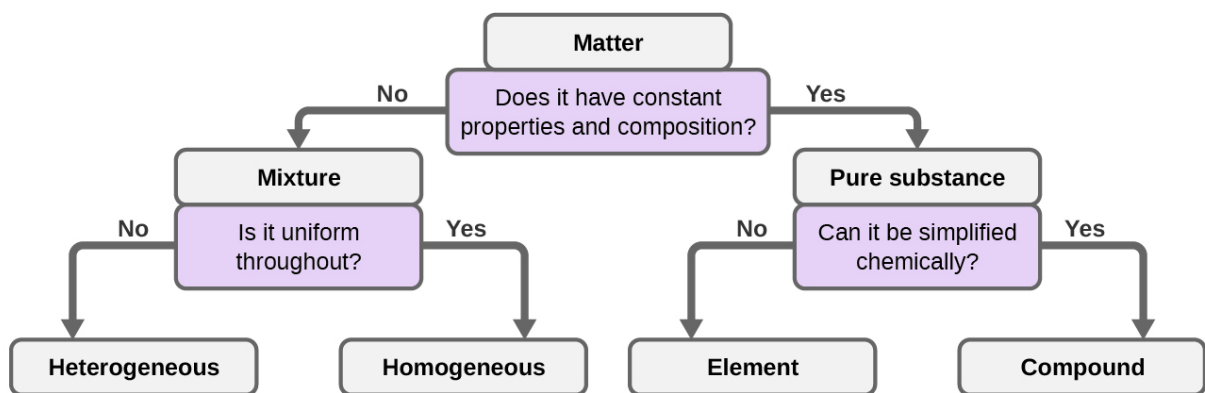
Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth's crust and atmosphere ([link]). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Elemental Composition of Earth						
Element	Symbol	Percent Mass		Element	Symbol	Percent Mass
oxygen	O	49.20		chlorine	Cl	0.19
silicon	Si	25.67		phosphorus	P	0.11
aluminum	Al	7.50		manganese	Mn	0.09
iron	Fe	4.71		carbon	C	0.08
calcium	Ca	3.39		sulfur	S	0.06
sodium	Na	2.63		barium	Ba	0.04
potassium	K	2.40		nitrogen	N	0.03

Elemental Composition of Earth						
Element	Symbol	Percent Mass		Element	Symbol	Percent Mass
magnesium	Mg	1.93		fluorine	F	0.03
hydrogen	H	0.87		strontium	Sr	0.02
titanium	Ti	0.58		all others	-	0.47

Note:

Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in ([link]).

Water
$2H_2O(l)$

Hydrogen
$2H_2(g)$

Oxygen
$O_2(g)$
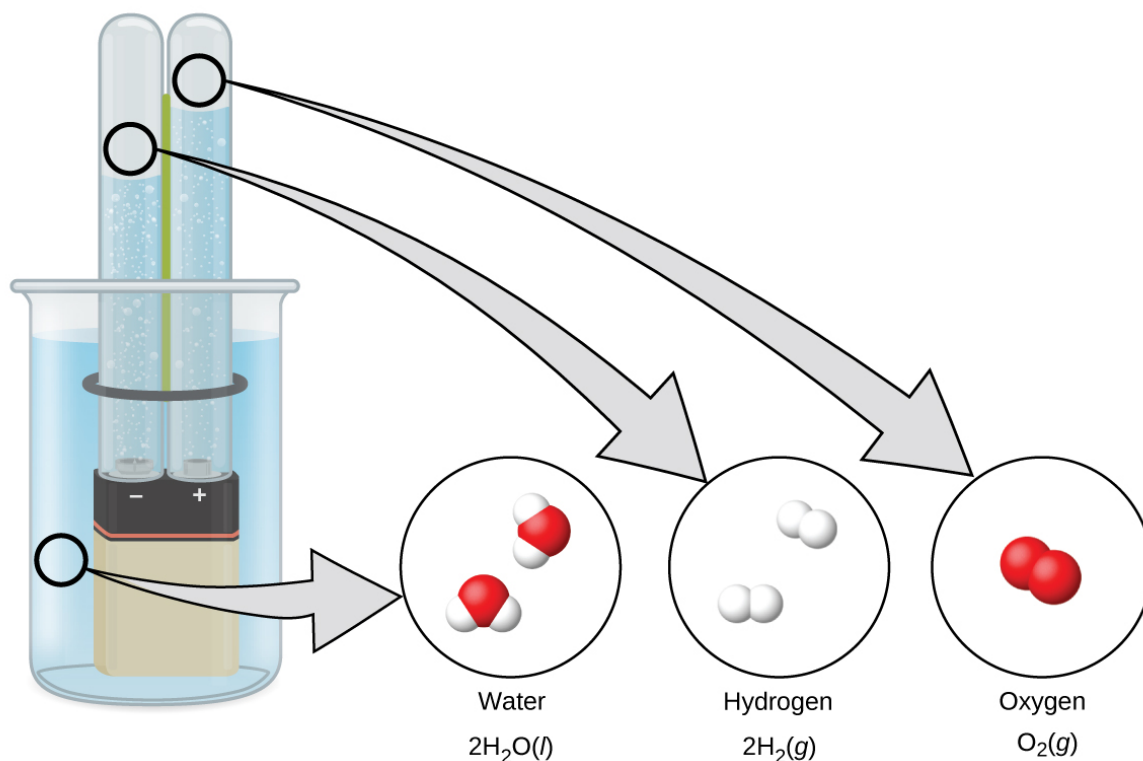
The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$, will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline ([link]). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.
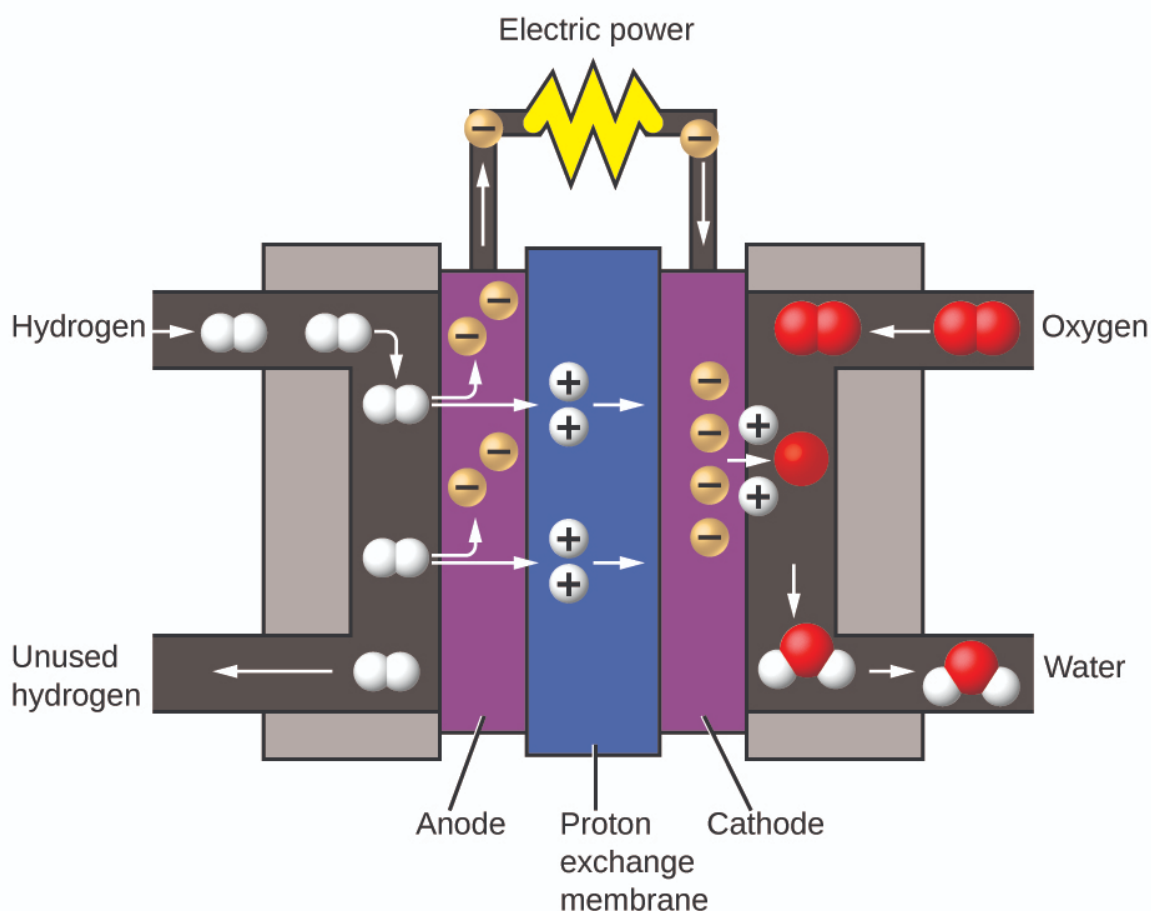
A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

Note:

Chemistry of Cell Phones

Imagine how different your life would be without cell phones ([link]) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.

Case components
Polymers such as ABS and/or metals such as aluminum, iron, magnesium

Screen components
Silicon oxide (glass) strengthened by addition of aluminum, sodium, potassium

Processor components
Silicon, common metals (copper, tin, gold), uncommon elements (yttrium, gadolinium)

Battery components
Lithium combined with other metals such as cobalt, iron, copper

Almost one-third of naturally occurring elements are used to make a cell phone. (credit: modification of work by John Taylor)

Key Concepts and Summary

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Why do we use an object's mass, rather than its weight, to indicate the amount of matter it contains?

Exercise:

Problem:

What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

Solution:

Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

Exercise:

Problem:

How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

Exercise:

Problem:

How does a homogeneous mixture differ from a pure substance? How are they similar?

Solution:

The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

Exercise:

Problem: How does an element differ from a compound? How are they similar?

Exercise:

Problem:

How do molecules of elements and molecules of compounds differ? In what ways are they similar?

Solution:

Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

Exercise:

Problem: How does an atom differ from a molecule? In what ways are they similar?

Exercise:

Problem:

Many of the items you purchase are mixtures of pure compounds. Select one of these commercial products and prepare a list of the ingredients that are pure compounds.

Solution:

Answers will vary. Sample answer: Gatorade contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

Exercise:

Problem: Classify each of the following as an element, a compound, or a mixture:

(a) copper

(b) water

(c) nitrogen

(d) sulfur

(e) air

(f) sucrose

(g) a substance composed of molecules each of which contains two iodine atoms

(h) gasoline

Exercise:

Problem: Classify each of the following as an element, a compound, or a mixture:

(a) iron

(b) oxygen

(c) mercury oxide

(d) pancake syrup

(e) carbon dioxide

(f) a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom

(g) baking soda

(h) baking powder

Solution:

(a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture

Exercise:

Problem: A sulfur atom and a sulfur molecule are not identical. What is the difference?

Exercise:

Problem:

How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

Solution:

In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

Exercise:

Problem: We refer to astronauts in space as weightless, but not without mass. Why?

Exercise:

Problem:

As we drive an automobile, we don't think about the chemicals consumed and produced. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.

Solution:

Gasoline (a mixture of compounds), oxygen, and to a lesser extent, nitrogen are consumed. Carbon dioxide and water are the principal products. Carbon monoxide and nitrogen oxides are produced in lesser amounts.

Exercise:

Problem:

Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.

Exercise:

Problem:

When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide which we call rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?

Solution:

(a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass. (b) 0.9 g

Exercise:

Problem:

As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:

(a) Exactly one pound of bread dough is placed in a baking tin. The dough is cooked in an oven at 350 °F releasing a wonderful aroma of freshly baked bread during the cooking process. Is the mass of the baked loaf less than, greater than, or the same as the one pound of original dough? Explain.

(b) When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.

(c) Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?

Exercise:

Problem:

Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

Equation:

$$\text{glucose} \longrightarrow \text{ethanol} + \text{carbon dioxide}$$
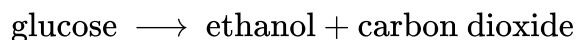
(a) If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?

(b) If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.

(c) If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?

Solution:

(a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g

Glossary

atom
    smallest particle of an element that can enter into a chemical combination

compound
    pure substance that can be decomposed into two or more elements

element
substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

gas
state in which matter has neither definite volume nor shape

heterogeneous mixture
combination of substances with a composition that varies from point to point

homogeneous mixture
(also, solution) combination of substances with a composition that is uniform throughout

liquid
state of matter that has a definite volume but indefinite shape

law of conservation of matter
when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

mass
fundamental property indicating amount of matter

matter
anything that occupies space and has mass

mixture
matter that can be separated into its components by physical means

molecule
bonded collection of two or more atoms of the same or different elements

plasma
gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pure substance
homogeneous substance that has a constant composition

solid
state of matter that is rigid, has a definite shape, and has a fairly constant volume

weight
force that gravity exerts on an object

Physical and Chemical Properties
By the end of this section, you will be able to:

- Identify properties of and changes in matter as physical or chemical
- Identify properties of matter as extensive or intensive

The characteristics that enable us to distinguish one substance from another are called properties. A **physical property** is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A **physical change** is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water ([link]). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.

(a)   (b)

(a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr)

The change of one type of matter into another type (or the inability to change) is a **chemical property**. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize ([link]). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.

(a)   (b)

(a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

To identify a chemical property, we look for a chemical change. A **chemical change** always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical

change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting ([link]).

(a)

(b)

(c)

(d)

(a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-

brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

Properties of matter fall into one of two categories. If the property depends on the amount of matter present, it is an **extensive property**. The mass and volume of a substance are examples of extensive properties; for instance, a gallon of milk has a larger mass and volume than a cup of milk. The value of an extensive property is directly proportional to the amount of matter in question. If the property of a sample of matter does not depend on the amount of matter present, it is an **intensive property**. Temperature is an example of an intensive property. If the gallon and cup of milk are each at 20 °C (room temperature), when they are combined, the temperature remains at 20 °C. As another example, consider the distinct but related properties of heat and temperature. A drop of hot cooking oil spattered on your arm causes brief, minor discomfort, whereas a pot of hot oil yields severe burns. Both the drop and the pot of oil are at the same temperature (an intensive property), but the pot clearly contains much more heat (extensive property).

Note:
Hazard Diamond
You may have seen the symbol shown in [link] on containers of chemicals in a laboratory or workplace. Sometimes called a "fire diamond" or "hazard diamond," this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.

4 Deadly
3 Extreme danger
2 Hazardous
1 Slightly hazardous
0 Normal material

Health hazard

Flash points:
4 Below 73 °F
3 Below 100 °F
2 Above 100 °F not exceeding 200 °F
1 Above 200 °F
0 Will not burn

Fire hazard

Reactivity

4 May detonate
3 Shock and heat may detonate
2 Violent chemical change
1 Unstable if heated
0 Stable

Specific hazard

OX   Oxidizer
ACID   Acid
ALK   Alkali
COR   Corrosive
₩   Use no water
☢   Radioactive

The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

The National Fire Protection Agency (NFPA) 704 Hazard Identification System was developed by NFPA to provide safety information about certain substances. The system details flammability, reactivity, health, and other hazards. Within the overall diamond symbol, the top (red) diamond specifies the level of fire hazard (temperature range for flash point). The blue (left) diamond indicates the level of health hazard. The yellow (right) diamond describes reactivity hazards, such as how readily the substance will undergo detonation or a violent chemical change. The white (bottom) diamond points out special hazards, such as if it is an oxidizer (which allows the substance to burn in the absence of air/oxygen), undergoes an unusual or dangerous reaction with water, is corrosive, acidic, alkaline, a biological hazard, radioactive, and so on. Each hazard is rated on a scale from 0 to 4, with 0 being no hazard and 4 being extremely hazardous.

While many elements differ dramatically in their chemical and physical properties, some elements have similar properties. We can identify sets of elements that exhibit common behaviors. For example, many elements conduct heat and electricity well, whereas others are poor conductors. These properties can be used to sort the elements into three classes: metals (elements that conduct well), nonmetals (elements that conduct poorly), and metalloids (elements that have properties of both metals and nonmetals).

The periodic table is a table of elements that places elements with similar properties close together ([link]). You will learn more about the periodic table as you continue your study of chemistry.

The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Key Concepts and Summary

All substances have distinct physical and chemical properties, and may undergo physical or chemical changes. Physical properties, such as hardness and boiling point, and physical changes, such as melting or freezing, do not involve a change in the composition of matter. Chemical properties, such flammability and acidity, and chemical changes, such as rusting, involve production of matter that differs from that present beforehand.

Measurable properties fall into one of two categories. Extensive properties depend on the amount of matter present, for example, the mass of gold. Intensive properties do not depend on the amount of matter present, for example, the density of gold. Heat is an example of an extensive property, and temperature is an example of an intensive property.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Classify the six underlined properties in the following paragraph as chemical or physical:

Fluorine is a pale yellow <u>gas</u> that <u>reacts with most substances</u>. The free element <u>melts at −220 °C</u> and <u>boils at −188 °C</u>. Finely divided <u>metals burn in fluorine</u> with a bright flame. <u>Nineteen grams of fluorine will react with 1.0 gram of hydrogen</u>.

Exercise:

Problem:

Classify each of the following changes as physical or chemical:

(a) condensation of steam

(b) burning of gasoline

(c) souring of milk

(d) dissolving of sugar in water

(e) melting of gold

Solution:

(a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical

Exercise:

Problem:

Classify each of the following changes as physical or chemical:

(a) coal burning

(b) ice melting

(c) mixing chocolate syrup with milk

(d) explosion of a firecracker

(e) magnetizing of a screwdriver

Exercise:

Problem:

The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?

Solution:

physical

Exercise:

Problem:

A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?

Exercise:

Problem:

Explain the difference between extensive properties and intensive properties.

Solution:

The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

Exercise:

Problem:

Identify the following properties as either extensive or intensive.

(a) volume

(b) temperature

(c) humidity

(d) heat

(e) boiling point

Exercise:

Problem:

The density (d) of a substance is an intensive property that is defined as the ratio of its mass (m) to its volume (V).

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \qquad d = \frac{m}{V}$$

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

Solution:

Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect "cancel" this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

Glossary

chemical change
>   change producing a different kind of matter from the original kind of matter

chemical property
>   behavior that is related to the change of one kind of matter into another kind of matter

extensive property
>   property of a substance that depends on the amount of the substance

intensive property
>   property of a substance that is independent of the amount of the substance

physical change
>   change in the state or properties of matter that does not involve a change in its chemical composition

physical property
characteristic of matter that is not associated with any change in its chemical composition

Introduction

class="introduction"

- Early Ideas in Atomic Theory
- Evolution of Atomic Theory
- Atomic Structure and Symbolism
- Chemical Formulas
- The Periodic Table
- Molecular and Ionic Compounds
- Chemical Nomenclature

Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)
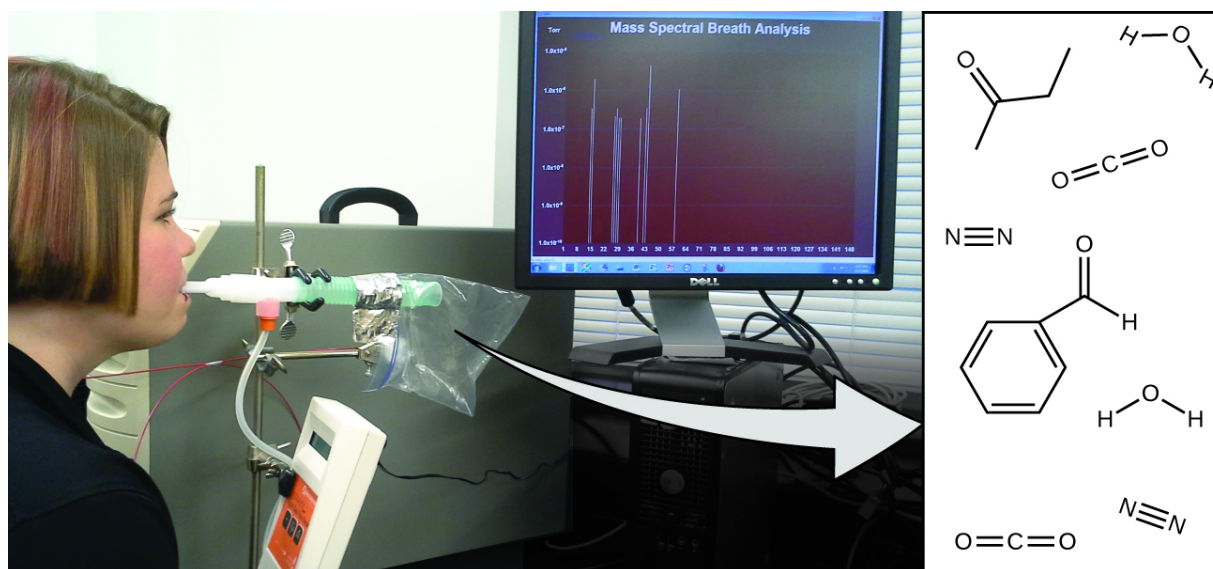
Your overall health and susceptibility to disease depends upon the complex interaction between your genetic makeup and environmental exposure, with the outcome difficult to predict. Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer. Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

Early Ideas in Atomic Theory
By the end of this section, you will be able to:

- State the postulates of Dalton's atomic theory
- Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The language used in chemistry is seen and heard in many disciplines, ranging from medicine to engineering to forensics to art. The language of chemistry includes its own vocabulary as well as its own form of shorthand. Chemical symbols are used to represent atoms and elements. Chemical formulas depict molecules as well as the composition of compounds. Chemical equations provide information about the quality and quantity of the changes associated with chemical reactions.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, the composition and mass of an atom, the variability of the composition of isotopes, ion formation, chemical bonds in ionic and covalent compounds, the types of chemical reactions, and the naming of compounds. We will also introduce one of the most powerful tools for organizing chemical knowledge: the periodic table.

Atomic Theory through the Nineteenth Century

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and "elements" as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained

using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of **Dalton's atomic theory**.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element ([link]). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.
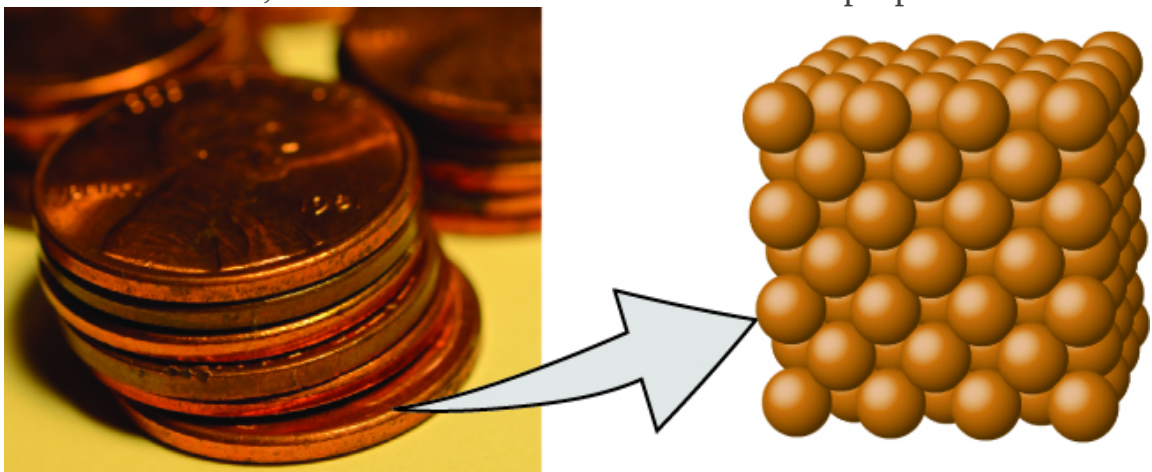
A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio ([link]).
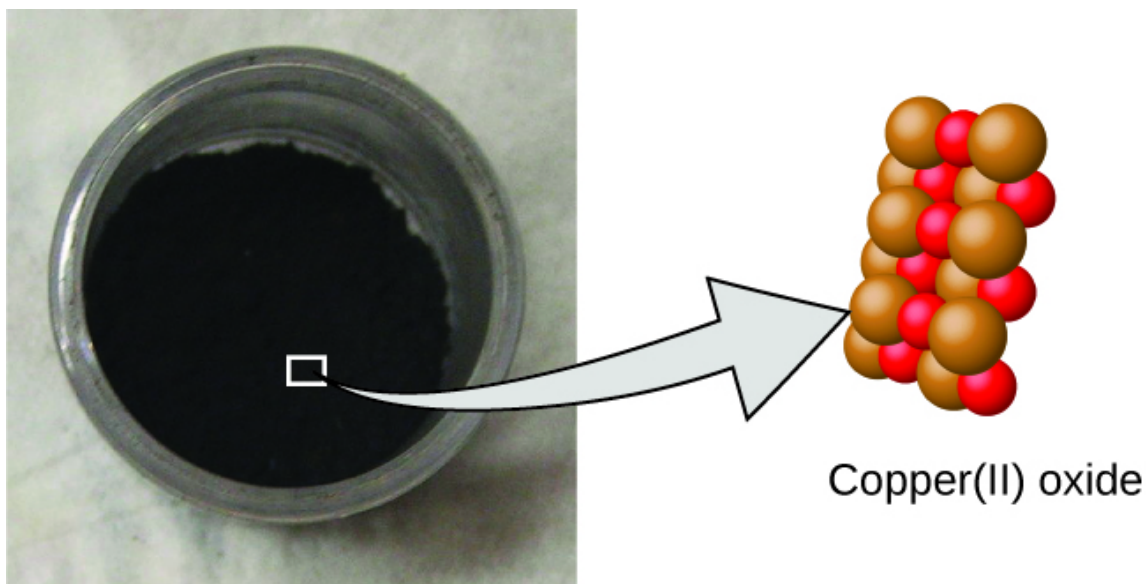
Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change ([link]).

The elements
copper and oxygen

The compound
copper(II) oxide
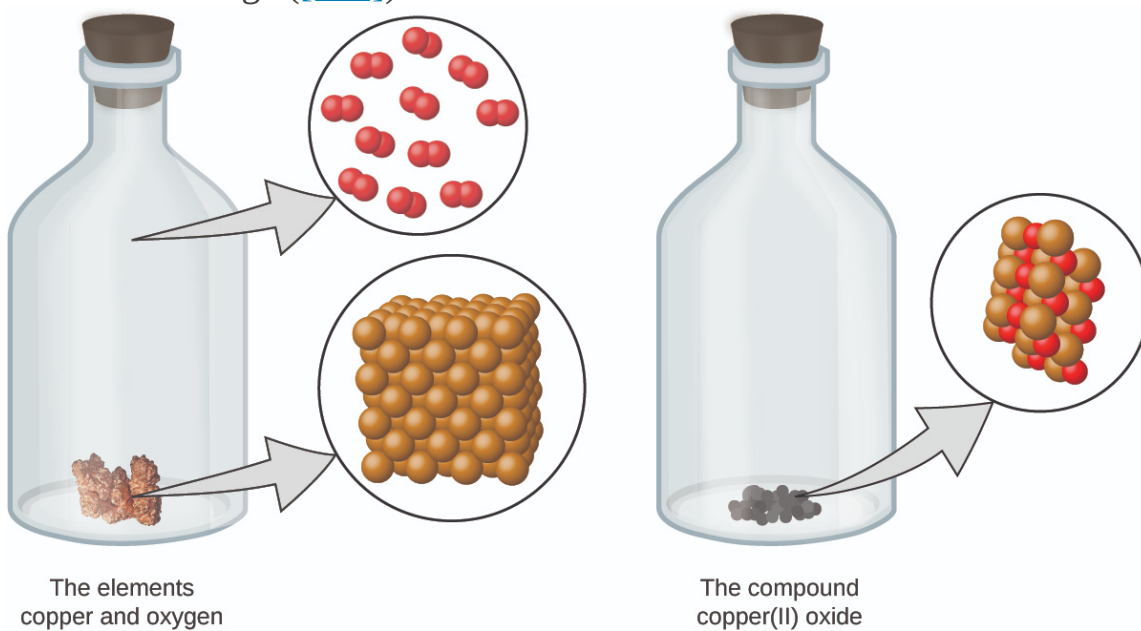
When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php)

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

Example:
Testing Dalton's Atomic Theory
In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

Starting materials   Products of the change
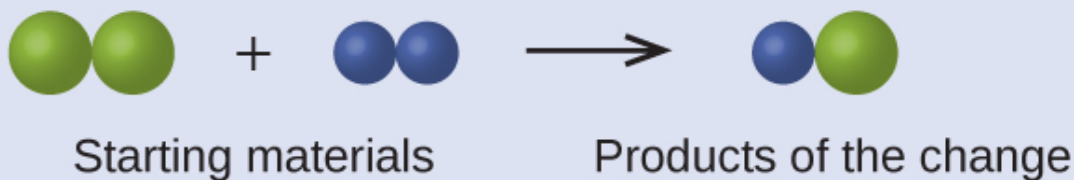
Solution
The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

Check Your Learning

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

Starting materials   Products of the change

Note:
Answer:
The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the **law of definite proportions** or the **law of constant composition**. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in [link].

Constant Composition of Isooctane			
Sample	**Carbon**	**Hydrogen**	**Mass Ratio**
A	14.82 g	2.78 g	$\dfrac{14.82 \text{ g carbon}}{2.78 \text{ g hydrogen}} = \dfrac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$
B	22.33 g	4.19 g	$\dfrac{22.33 \text{ g carbon}}{4.19 \text{ g hydrogen}} = \dfrac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$
C	19.40 g	3.64 g	$\dfrac{19.40 \text{ g carbon}}{3.63 \text{ g hydrogen}} = \dfrac{5.33 \text{ g carbon}}{1.00 \text{ g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The **law of multiple proportions** states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.
Equation:

$$\frac{\dfrac{1.116 \text{ g Cl}}{1 \text{ g Cu}}}{\dfrac{0.558 \text{ g Cl}}{1 \text{ g Cu}}} = \frac{2}{1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 ([link]).
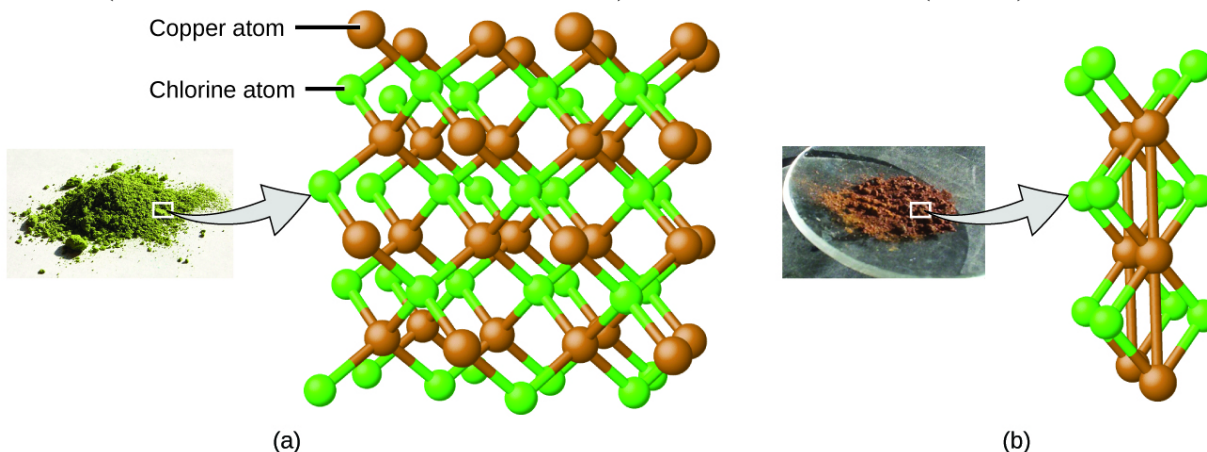
Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

Example:
Laws of Definite and Multiple Proportions
A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?
Solution
In compound A, the mass ratio of carbon to oxygen is:
Equation:

$$\frac{1.33 \text{ g O}}{1 \text{ g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

Equation:

$$\frac{2.67 \text{ g O}}{1 \text{ g C}}$$

The ratio of these ratios is:

Equation:

$$\frac{\frac{1.33 \text{ g O}}{1 \text{ g C}}}{\frac{2.67 \text{ g O}}{1 \text{ g C}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much oxygen per amount of carbon) as B. A possible pair of compounds that would fit this relationship would be A = CO_2 and B = CO.

Check Your Learning

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Note:

Answer:

In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13 \text{ g C}}{2.96 \text{ g H}}$. In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91 \text{ g C}}{3.34 \text{ g H}}$. The ratio of these ratios is $\frac{\frac{14.13 \text{ g C}}{2.96 \text{ g H}}}{\frac{19.91 \text{ g C}}{3.34 \text{ g H}}} = \frac{4.77 \text{ g C/g H}}{5.96 \text{ g C/g H}} = 0.800 = \frac{4}{5}$. This small, whole-

number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

Key Concepts and Summary

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

Chemistry End of Chapter Exercises

Exercise:

Problem:

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?
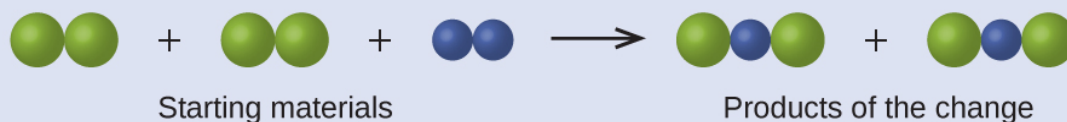

Starting materials   Products of the change
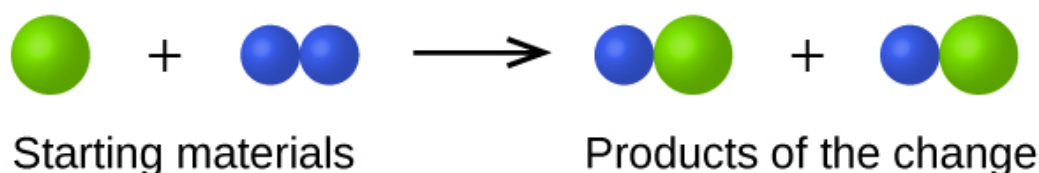
Solution:

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that that atoms are not created during a chemical change, but are merely redistributed.

Exercise:

Problem:

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

Exercise:

Problem:

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

Solution:

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

Exercise:

Problem:

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

Glossary

Dalton's atomic theory
    set of postulates that established the fundamental properties of atoms

law of constant composition
    (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of definite proportions
    (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions
    when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Evolution of Atomic Theory
By the end of this section, you will be able to:

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Define isotopes and give examples for several elements

In the two centuries since Dalton developed his ideas, scientists have made significant progress in furthering our understanding of atomic theory. Much of this came from the results of several seminal experiments that revealed the details of the internal structure of atoms. Here, we will discuss some of those key developments, with an emphasis on application of the scientific method, as well as understanding how the experimental evidence was analyzed. While the historical persons and dates behind these experiments can be quite interesting, it is most important to understand the concepts resulting from their work.

Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms ([link]).
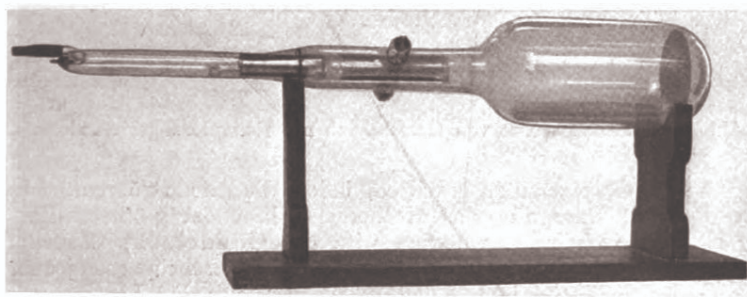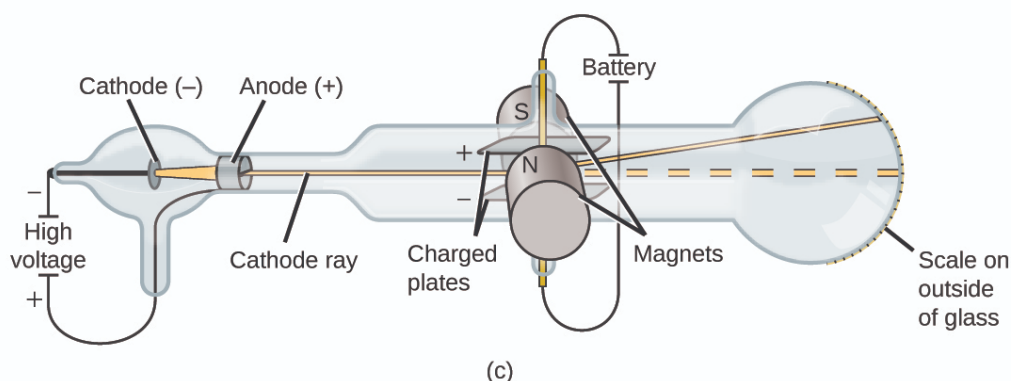
(a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons)

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an **electron**, a negatively charged, subatomic

particle with a mass more than one thousand-times less that of an atom. The term "electron" was coined in 1891 by Irish physicist George Stoney, from "*electr*ic i*on.*"

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops ([link]).
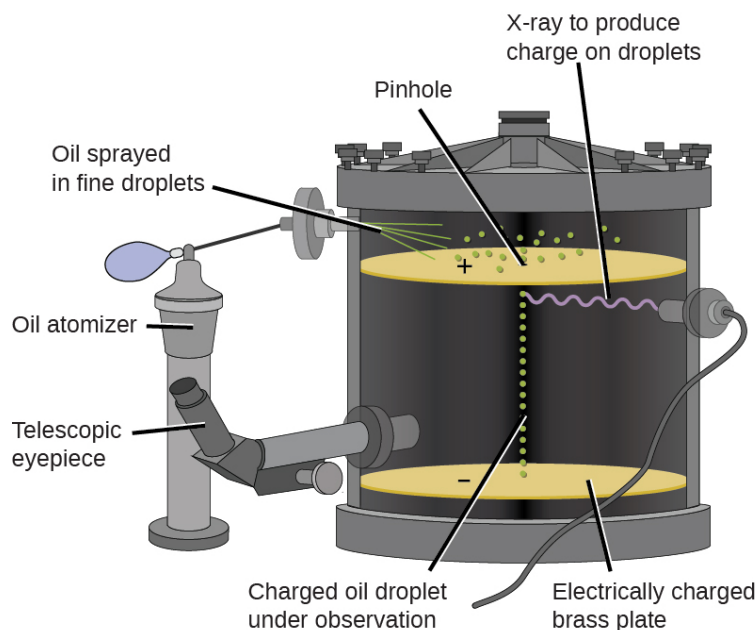
Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.
Equation:

$$\text{Mass of electron} = 1.602 \times 10^{-19}\,\text{C} \times \frac{1\,\text{kg}}{1.759 \times 10^{11}\,\text{C}} = 9.107 \times 10^{-31}\,\text{kg}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the "plum pudding" model of atoms, which described a positively charged

mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons ([link]).
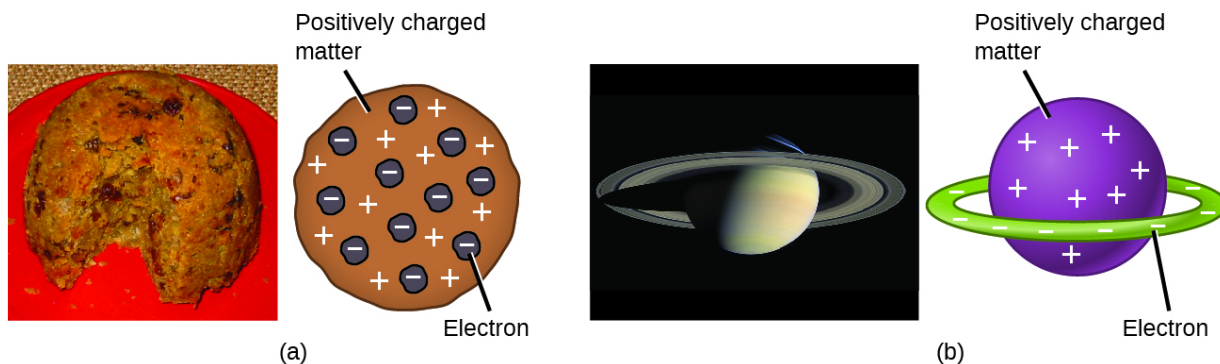
(a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons)

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged **alpha particles (α particles)** that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source ([link]). Rutherford described finding these results: "It was quite the most incredible event that has ever happened

to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you"[footnote] (p. 68).

Ernest Rutherford, "The Development of the Theory of Atomic Structure," ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/items/backgroundtomode032734mbp/backgroundtomode032734mbp.pdf.
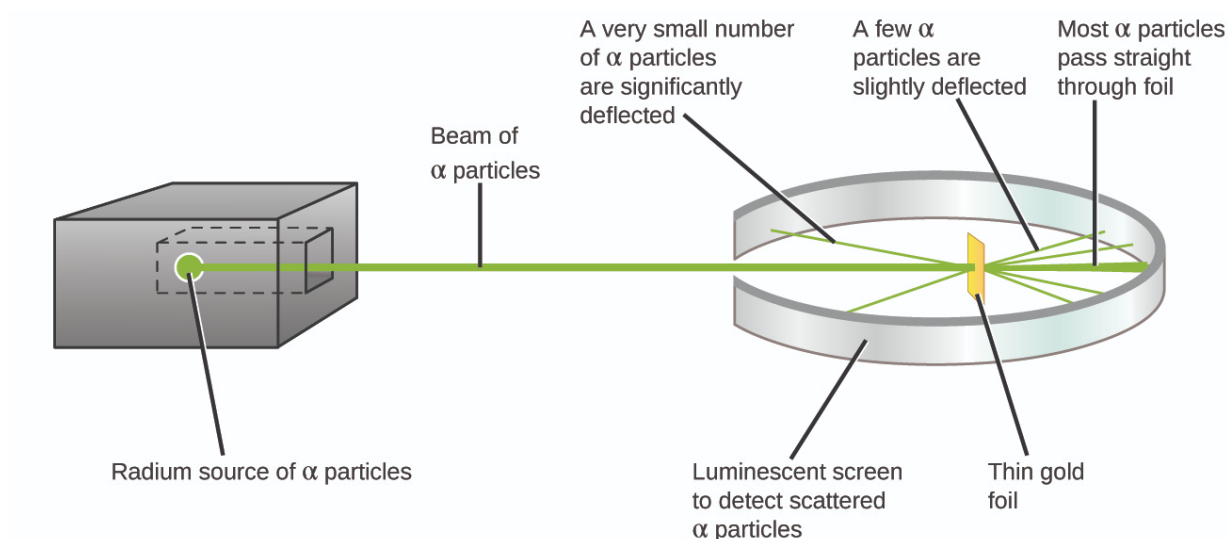
Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the **nucleus**, must be at the center of each atom.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral ([link]). After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the **proton**, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

Most α particles are not deflected

A very small number of α particles are significantly deflected

A few α particles are slightly deflected

Nucleus of gold atom

Gold foil

Enlarged cross-section
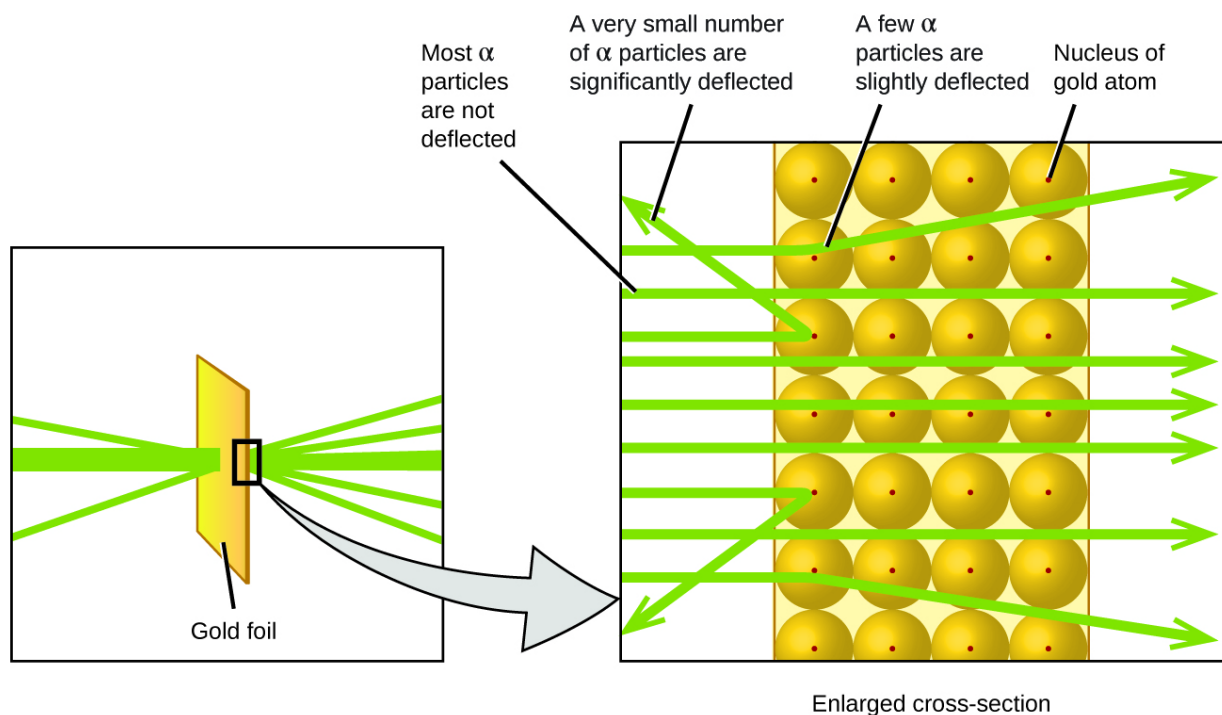
The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

Note:

The Rutherford Scattering simulation allows you to investigate the differences between a "plum pudding" atom and a Rutherford atom by firing α particles at each type of atom.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called **isotopes**—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of **neutrons**, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

Key Concepts and Summary

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called electrons. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford's gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons. Soddy demonstrated that atoms of the same element can differ in mass; these are called isotopes.

Chemistry End of Chapter Exercises

Exercise:

Problem:

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

Solution:

Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

Exercise:

Problem: How are electrons and protons similar? How are they different?

Exercise:

Problem: How are protons and neutrons similar? How are they different?

Solution:

Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

Exercise:

Problem:

Predict and test the behavior of α particles fired at a "plum pudding" model atom.

(a) Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles

Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

Exercise:

Problem:

Predict and test the behavior of α particles fired at a Rutherford atom model.

(a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.

(b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.

(c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?

(d) Now test your predictions from (a), (b), and (c). Open the [Rutherford Scattering simulation](#) and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

Solution:

(a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller —both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

Glossary

alpha particle (α particle)
    positively charged particle consisting of two protons and two neutrons

electron
    negatively charged, subatomic particle of relatively low mass located outside the nucleus

isotopes
    atoms that contain the same number of protons but different numbers of neutrons

neutron
    uncharged, subatomic particle located in the nucleus

nucleus
    massive, positively charged center of an atom made up of protons and neutrons

proton
    positively charged, subatomic particle located in the nucleus

Atomic Structure and Symbolism
By the end of this section, you will be able to:

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium ([link]).
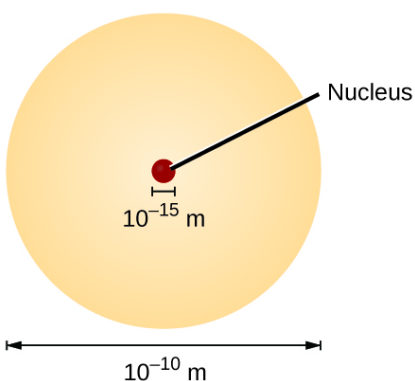
If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the **atomic mass unit (amu)** and the **fundamental unit of charge (e)**. The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly $\frac{1}{12}$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The **Dalton (Da)** and the **unified atomic mass unit (u)** are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in [link]. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00

amu. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Properties of Subatomic Particles					
Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	$1-$	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	$1+$	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

The number of protons in the nucleus of an atom is its **atomic number (Z)**. This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its **mass number (A)**. The number of neutrons is therefore the difference between the mass number and the atomic number: A − Z = number of neutrons.

Equation:

$$
\begin{aligned}
\text{atomic number (Z)} &= \text{number of protons} \\
\text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\
\text{A} - \text{Z} &= \text{number of neutrons}
\end{aligned}
$$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an **ion**. The charge of an atom is defined as follows:

Atomic charge = number of protons − number of electrons

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an **anion**. Positively charged atoms called **cations** are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2− charge (8 − 10 = 2−).

Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland ([link]).

(a)   (b)

(a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 − 53 = 74). Since the iodine is added as a 1− anion, the number of electrons is 54 [53 – (1–) = 54].

Check Your Learning

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Note:

Answer:

78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A **chemical symbol** is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg ([link]). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).

The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The symbols for several common elements and their atoms are listed in [link]. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table in [link] (also found in [link]).

Some Common Elements and Their Symbols			
Element	**Symbol**	**Element**	**Symbol**
aluminum	Al	iron	Fe (from *ferrum*)

Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists (or occasionally locations); for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

Note:

Visit this site to learn more about IUPAC, the International Union of Pure and Applied Chemistry, and explore its periodic table.

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol ([link]). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

Mass number —— 4   2+ —— Charge   24   2+

He   Mg

Atomic number — 2   12
(often omitted)
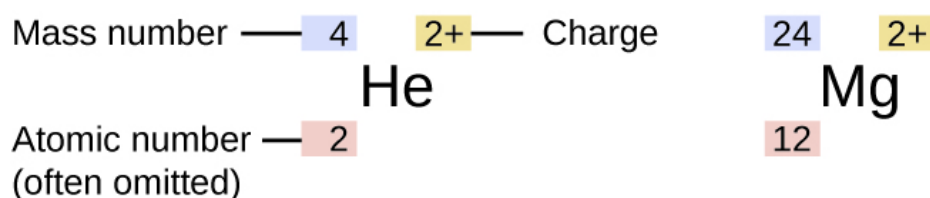
The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in [link]. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Nuclear Compositions of Atoms of the Very Light Elements						
Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^1_1$H (protium)	1	1	0	1.0078	99.989
	$^2_1$H (deuterium)	1	1	1	2.0141	0.0115

Nuclear Compositions of Atoms of the Very Light Elements						
Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
	$^{3}_{1}H$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}He$	2	2	1	3.01603	0.00013
	$^{4}_{2}He$	2	2	2	4.0026	100
lithium	$^{6}_{3}Li$	3	3	3	6.0151	7.59
	$^{7}_{3}Li$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}Be$	4	4	5	9.0122	100
boron	$^{10}_{5}B$	5	5	5	10.0129	19.9
	$^{11}_{5}B$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}C$	6	6	6	12.0000	98.89
	$^{13}_{6}C$	6	6	7	13.0034	1.11
	$^{14}_{6}C$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}N$	7	7	7	14.0031	99.63
	$^{15}_{7}N$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}O$	8	8	8	15.9949	99.757
	$^{17}_{8}O$	8	8	9	16.9991	0.038
	$^{18}_{8}O$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}F$	9	9	10	18.9984	100
neon	$^{20}_{10}Ne$	10	10	10	19.9924	90.48
	$^{21}_{10}Ne$	10	10	11	20.9938	0.27
	$^{22}_{10}Ne$	10	10	12	21.9914	9.25

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the **atomic mass** of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

Equation:

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

Equation:

$$\begin{aligned}
\text{boron average mass} &= (0.199 \times 10.0129 \text{ amu}) + (0.801 \times 11.0093 \text{ amu}) \\
&= 1.99 \text{ amu} + 8.82 \text{ amu} \\
&= 10.81 \text{ amu}
\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Example:

Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

Equation:

$$\begin{aligned}
\text{average mass} \ &= (0.9184 \ \times \ 19.9924 \text{ amu}) + (0.0047 \ \times \ 20.9940 \text{ amu}) + (0.0769 \ \times \ 21.9914 \text{ amu}) \\
&= (18.36 + 0.099 + 1.69) \text{ amu} \\
&= 20.15 \text{ amu}
\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

Check Your Learning

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Note:
Answer:

24.31 amu

Note:

Visit this site to make mixtures of the main isotopes of the first 18 elements, gain experience with average atomic mass, and check naturally occurring isotope ratios using the Isotopes and Atomic Mass simulation.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer ([link]), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.
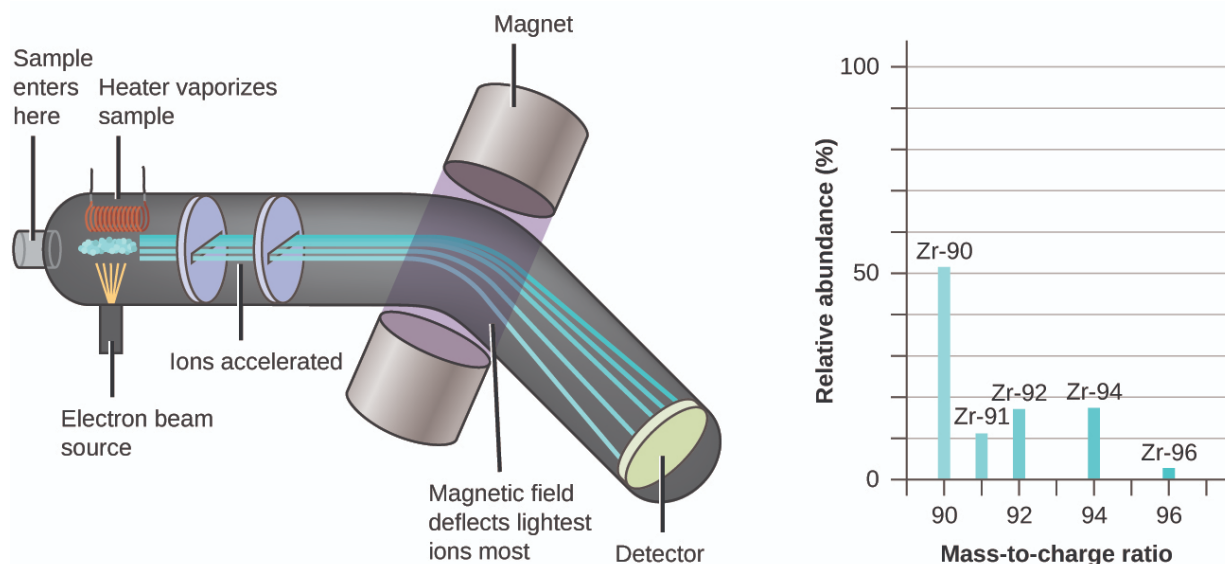
Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

Note:

See an animation that explains mass spectrometry. Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.

Key Concepts and Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $\frac{1}{12}$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

Key Equations

- average mass $= \sum_{i} (\text{fractional abundance} \times \text{isotopic mass})_i$

Chemistry End of Chapter Exercises

Exercise:

  Problem:

  In what way are isotopes of a given element always different? In what way(s) are they always the same?

Exercise:

  Problem: Write the symbol for each of the following ions:

  (a) the ion with a 1+ charge, atomic number 55, and mass number 133

  (b) the ion with 54 electrons, 53 protons, and 74 neutrons

  (c) the ion with atomic number 15, mass number 31, and a 3− charge

  (d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

  Solution:

  (a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

Exercise:

  Problem: Write the symbol for each of the following ions:

  (a) the ion with a 3+ charge, 28 electrons, and a mass number of 71

  (b) the ion with 36 electrons, 35 protons, and 45 neutrons

  (c) the ion with 86 electrons, 142 neutrons, and a 4+ charge

  (d) the ion with a 2+ charge, atomic number 38, and mass number 87

Exercise:

  Problem: Open the Build an Atom simulation and click on the Atom icon.

  (a) Pick any one of the first 10 elements that you would like to build and state its symbol.

(b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element. State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.

(c) Click on "Net Charge" and "Mass Number," check your answers to (b), and correct, if needed.

(d) Predict whether your atom will be stable or unstable. State your reasoning.

(e) Check the "Stable/Unstable" box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

Solution:

(a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

Exercise:

Problem: Open the [Build an Atom simulation](#)

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.

(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

Exercise:

Problem: Open the [Build an Atom simulation](#)

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

Solution:

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^{6}Li or $^6_3$Li. (b) $^6\text{Li}^+$ or $^6_3\text{Li}^+$

Exercise:

Problem:

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

(a) atomic number 9, mass number 18, charge of 1−

(b) atomic number 43, mass number 99, charge of 7+

(c) atomic number 53, atomic mass number 131, charge of 1−

(d) atomic number 81, atomic mass number 201, charge of 1+

(e) Name the elements in parts (a), (b), (c), and (d).

Exercise:

Problem:

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

(a) atomic number 26, mass number 58, charge of 2+

(b) atomic number 53, mass number 127, charge of 1−

Solution:

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

Exercise:

Problem:

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{10}_{5}\text{B}$

(b) $^{199}_{80}\text{Hg}$

(c) $^{63}_{29}\text{Cu}$

(d) $^{13}_{6}\text{C}$

(e) $^{77}_{34}\text{Se}$

Exercise:

Problem:

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{7}_{3}\text{Li}$

(b) $^{125}_{52}\text{Te}$

(c) $^{109}_{47}\text{Ag}$

(d) $^{15}_{7}\text{N}$

(e) $^{31}_{15}\text{P}$

Solution:

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

Exercise:

Problem:

Click on the site and select the "Mix Isotopes" tab, hide the "Percent Composition" and "Average Atomic Mass" boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on "More" and then move the sliders to the appropriate amounts.

(d) Reveal the "Percent Composition" and "Average Atomic Mass" boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select "Nature's" mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match "Nature's" amounts as closely as possible.

Exercise:

Problem: Repeat [link] using an element that has three naturally occurring isotopes.

Solution:

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature's mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

Exercise:

Problem:

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

Exercise:

Problem:

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu) and abundances (50.69% and 49.31%) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

Solution:

79.904 amu

Exercise:

Problem:

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.

Exercise:

Problem:

The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

Glossary

anion
    negatively charged atom or molecule (contains more electrons than protons)

atomic mass
    average mass of atoms of an element, expressed in amu

atomic mass unit (amu)
    (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z)
    number of protons in the nucleus of an atom

cation
    positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol
    one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)
    alternative unit equivalent to the atomic mass unit

fundamental unit of charge
    (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C

ion
    electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)
    sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)
    alternative unit equivalent to the atomic mass unit

Chemical Formulas
By the end of this section, you will be able to:

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The **structural formula** for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule ([link]). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.
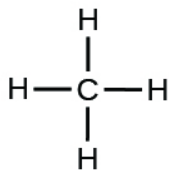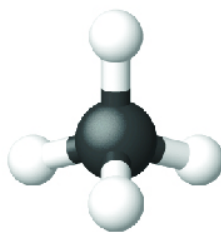
A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 ([link]).
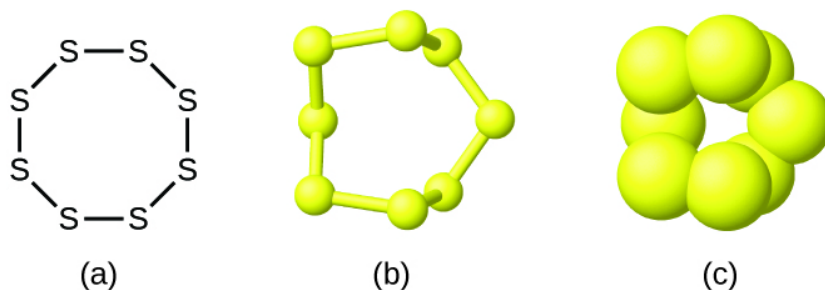
A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen ([link]).
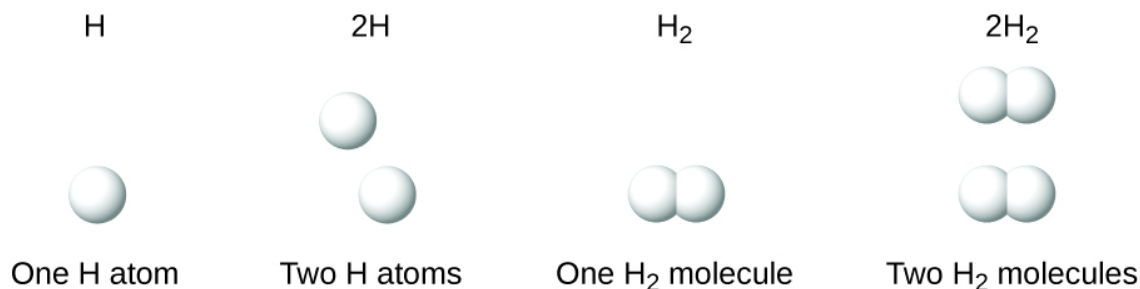
The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an **empirical formula**, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium ([link]).
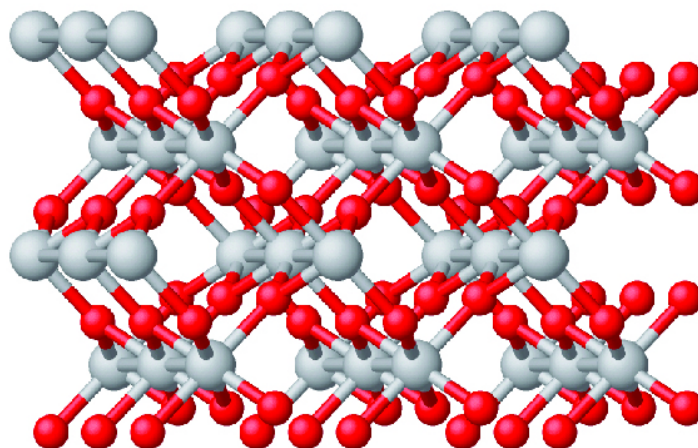
(a) The white compound titanium dioxide provides effective protection

from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by "osseous"/Flickr)

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 ([link]).
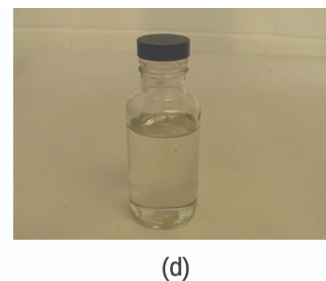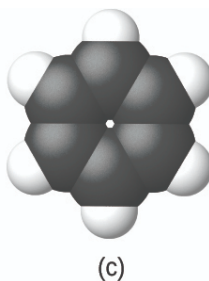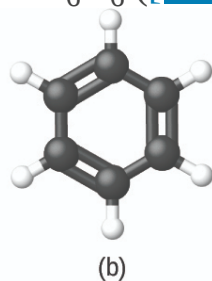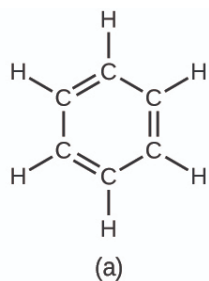
Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular

formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid ([link]) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.
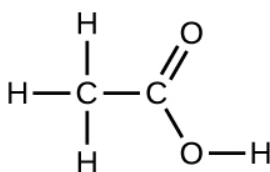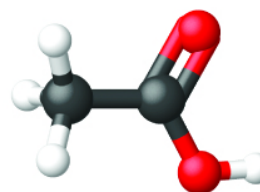
(a)   (b)   (c)

(a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Example:
Empirical and Molecular Formulas
Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?
Solution
The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

Check Your Learning

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Note:
Answer:

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

Note:

You can explore [molecule building](#) using an online simulation.

Note:

Lee Cronin

What is it that chemists do? According to Lee Cronin ([link]), chemists make very complicated molecules by "chopping up" small molecules and "reverse engineering" them. He wonders if we could "make a really cool universal chemistry set" by what he calls "app-ing" chemistry. Could we "app" chemistry?

In a 2012 TED talk, Lee describes one fascinating possibility: combining a collection of chemical "inks" with a 3D printer capable of fabricating a

reaction apparatus (tiny test tubes, beakers, and the like) to fashion a "universal toolkit of chemistry." This toolkit could be used to create custom-tailored drugs to fight a new superbug or to "print" medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, "What Apple did for music, I'd like to do for the discovery and distribution of prescription drugs."[footnote] View his full talk at the TED website.

Lee Cronin, "Print Your Own Medicine," Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.

Chemist Lee Cronin has been named one of the UK's 10 most inspirational scientists. The youngest chair at the University of

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $C_2H_4O_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form a methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of **isomers**—compounds with the same chemical formula but different molecular structures ([link]). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.
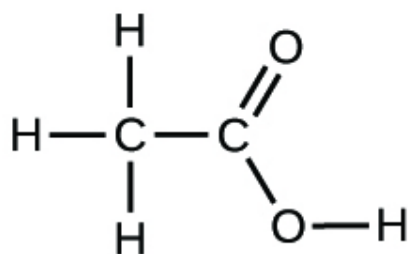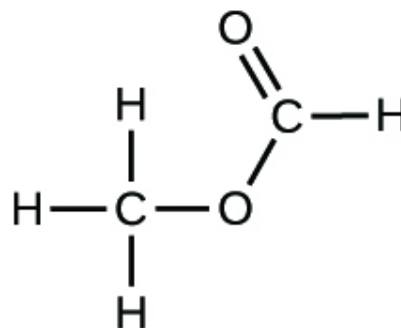
Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist ([link]). Acetic acid and methyl formate are **structural isomers**, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of **spatial isomers**, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(−)-carvone smells like spearmint.
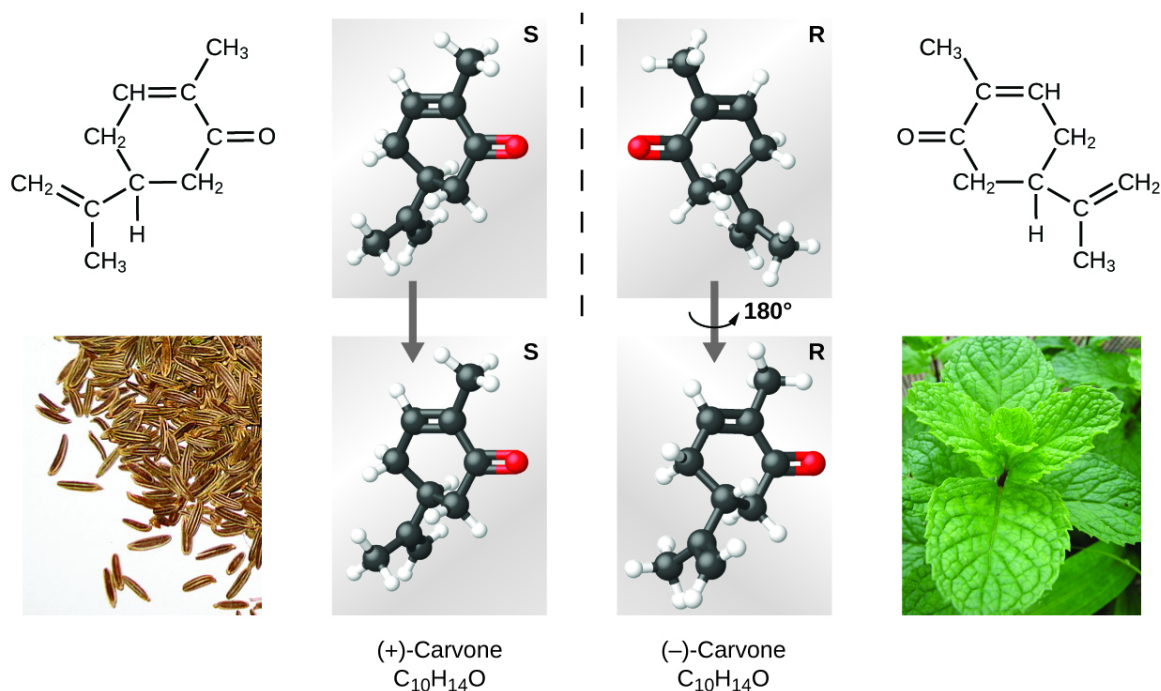
Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Note:

Select this link to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled "Mirror Molecule: Carvone").

Key Concepts and Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

Solution:

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

Exercise:

Problem:

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

Exercise:

Problem:

Write the molecular and empirical formulas of the following compounds:

(a)

$$O=C=O$$

(b)

$$H-C\equiv C-H$$

(c)
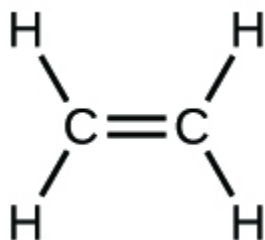
(d)
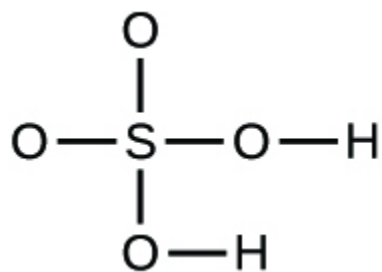
Solution:

(a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

Exercise:

Problem:

Write the molecular and empirical formulas of the following compounds:

(a)

(b)

(c)

(d)

$$\begin{array}{c}
\text{O}-\text{H} \\
| \\
\text{O}-\text{P}-\text{O}-\text{H} \\
| \\
\text{O}-\text{H}
\end{array}$$
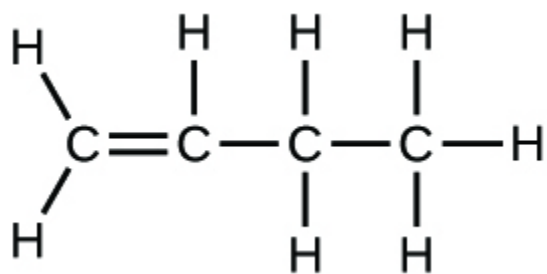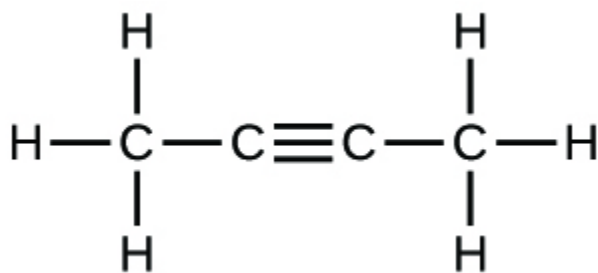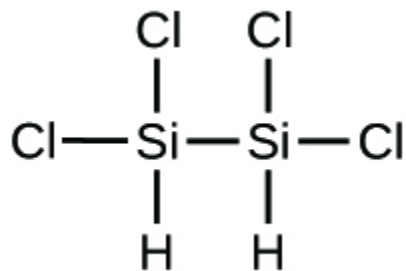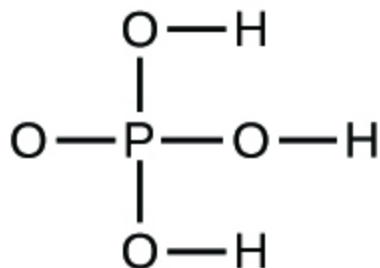
Exercise:

  Problem:

  Determine the empirical formulas for the following compounds:

  (a) caffeine, $C_8H_{10}N_4O_2$

  (b) fructose, $C_{12}H_{22}O_{11}$

  (c) hydrogen peroxide, H_2O_2

  (d) glucose, $C_6H_{12}O_6$

  (e) ascorbic acid (vitamin C), $C_6H_8O_6$

  Solution:

  (a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

Exercise:

  Problem:

  Determine the empirical formulas for the following compounds:

  (a) acetic acid, $C_2H_4O_2$

  (b) citric acid, $C_6H_8O_7$

  (c) hydrazine, N_2H_4

  (d) nicotine, $C_{10}H_{14}N_2$

(e) butane, C_4H_{10}

Exercise:

Problem: Write the empirical formulas for the following compounds:

(a)

H   O
| ||
H—C—C—O—H
|
H

(b)

H   O   H   H
| || | |
H—C—C—O—C—C—H
| | |
H   H   H
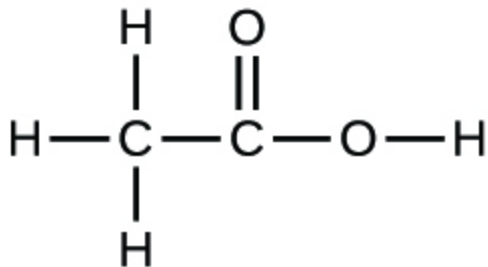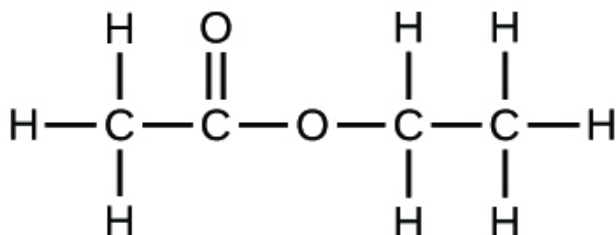
Solution:

(a) CH_2O; (b) C_2H_4O

Exercise:

Problem:

Open the [Build a Molecule simulation](#) and select the "Larger Molecules" tab. Select an appropriate atoms "Kit" to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the "Kit" to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on "3D" to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms in any way to make a different compound?

Exercise:

Problem:

Use the [Build a Molecule simulation](#) to repeat [link], but build a molecule with two carbons, six hydrogens, and one oxygen.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).

Solution:

(a) ethanol
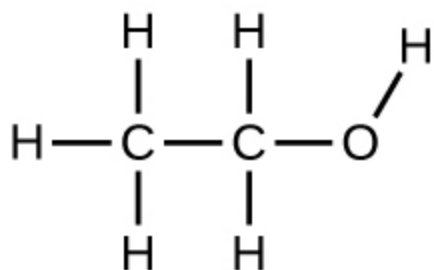
(b) methoxymethane, more commonly known as dimethyl ether
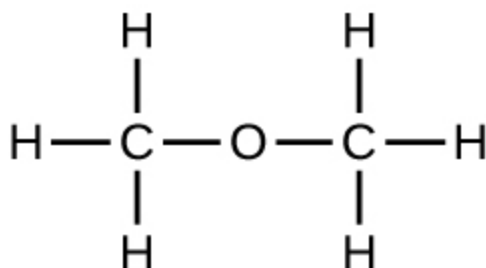
(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

Exercise:

Problem:

Use the Build a Molecule simulation to repeat [link], but build a molecule with three carbons, seven hydrogens, and one chlorine.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

Glossary

empirical formula
    formula showing the composition of a compound given as the simplest whole-number ratio of atoms

isomers
    compounds with the same chemical formula but different structures

molecular formula
    formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

spatial isomers
    compounds in which the relative orientations of the atoms in space differ

structural formula
    shows the atoms in a molecule and how they are connected

structural isomer
    one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

The Periodic Table
By the end of this section, you will be able to:

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized ([link]).

	Gruppo I. R²O	Gruppo II. RO	Gruppo III. R²O³	Gruppo IV. RH⁴ RO²	Gruppo V. RH³ R²O⁵	Gruppo VI. RH² RO³	Gruppo VII. RH R²O⁷	Gruppo VIII. RO⁴
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(a)   (b)

(a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column ([link]). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

Periodic Table of the Elements

| Period | | | | | | | | | | | | | | | | | | |

Group

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |

Period 1
- 1 **H** 1.008 hydrogen
- 2 **He** 4.003 helium

Period 2
- 3 **Li** 6.94 lithium
- 4 **Be** 9.012 beryllium
- 5 **B** 10.81 boron
- 6 **C** 12.01 carbon
- 7 **N** 14.01 nitrogen
- 8 **O** 16.00 oxygen
- 9 **F** 19.00 fluorine
- 10 **Ne** 20.18 neon

Period 3
- 11 **Na** 22.99 sodium
- 12 **Mg** 24.31 magnesium
- 13 **Al** 26.98 aluminum
- 14 **Si** 28.09 silicon
- 15 **P** 30.97 phosphorus
- 16 **S** 32.06 sulfur
- 17 **Cl** 35.45 chlorine
- 18 **Ar** 39.95 argon

Period 4
- 19 **K** 39.10 potassium
- 20 **Ca** 40.08 calcium
- 21 **Sc** 44.96 scandium
- 22 **Ti** 47.87 titanium
- 23 **V** 50.94 vanadium
- 24 **Cr** 52.00 chromium
- 25 **Mn** 54.94 manganese
- 26 **Fe** 55.85 iron
- 27 **Co** 58.93 cobalt
- 28 **Ni** 58.69 nickel
- 29 **Cu** 63.55 copper
- 30 **Zn** 65.38 zinc
- 31 **Ga** 69.72 gallium
- 32 **Ge** 72.63 germanium
- 33 **As** 74.92 arsenic
- 34 **Se** 78.97 selenium
- 35 **Br** 79.90 bromine
- 36 **Kr** 83.80 krypton

Period 5
- 37 **Rb** 85.47 rubidium
- 38 **Sr** 87.62 strontium
- 39 **Y** 88.91 yttrium
- 40 **Zr** 91.22 zirconium
- 41 **Nb** 92.91 niobium
- 42 **Mo** 95.95 molybdenum
- 43 **Tc** [97] technetium
- 44 **Ru** 101.1 ruthenium
- 45 **Rh** 102.9 rhodium
- 46 **Pd** 106.4 palladium
- 47 **Ag** 107.9 silver
- 48 **Cd** 112.4 cadmium
- 49 **In** 114.8 indium
- 50 **Sn** 118.7 tin
- 51 **Sb** 121.8 antimony
- 52 **Te** 127.6 tellurium
- 53 **I** 126.9 iodine
- 54 **Xe** 131.3 xenon

Period 6
- 55 **Cs** 132.9 cesium
- 56 **Ba** 137.3 barium
- 57-71 **La–Lu** *
- 72 **Hf** 178.5 hafnium
- 73 **Ta** 180.9 tantalum
- 74 **W** 183.8 tungsten
- 75 **Re** 186.2 rhenium
- 76 **Os** 190.2 osmium
- 77 **Ir** 192.2 iridium
- 78 **Pt** 195.1 platinum
- 79 **Au** 197.0 gold
- 80 **Hg** 200.6 mercury
- 81 **Tl** 204.4 thallium
- 82 **Pb** 207.2 lead
- 83 **Bi** 209.0 bismuth
- 84 **Po** [209] polonium
- 85 **At** [210] astatine
- 86 **Rn** [222] radon

Period 7
- 87 **Fr** [223] francium
- 88 **Ra** [226] radium
- 89-103 **Ac–Lr** **
- 104 **Rf** [267] rutherfordium
- 105 **Db** [270] dubnium
- 106 **Sg** [271] seaborgium
- 107 **Bh** [270] bohrium
- 108 **Hs** [277] hassium
- 109 **Mt** [276] meitnerium
- 110 **Ds** [281] darmstadtium
- 111 **Rg** [282] roentgenium
- 112 **Cn** [285] copernicium
- 113 **Uut** [285] ununtrium
- 114 **Fl** [289] flerovium
- 115 **Uup** [288] ununpentium
- 116 **Lv** [293] livermorium
- 117 **Uus** [294] ununseptium
- 118 **Uuo** [294] ununoctium

*
- 57 **La** 138.9 lanthanum
- 58 **Ce** 140.1 cerium
- 59 **Pr** 140.9 praseodymium
- 60 **Nd** 144.2 neodymium
- 61 **Pm** [145] promethium
- 62 **Sm** 150.4 samarium
- 63 **Eu** 152.0 europium
- 64 **Gd** 157.3 gadolinium
- 65 **Tb** 158.9 terbium
- 66 **Dy** 162.5 dysprosium
- 67 **Ho** 164.9 holmium
- 68 **Er** 167.3 erbium
- 69 **Tm** 168.9 thulium
- 70 **Yb** 173.1 ytterbium
- 71 **Lu** 175.0 lutetium

**
- 89 **Ac** [227] actinium
- 90 **Th** 232.0 thorium
- 91 **Pa** 231.0 protactinium
- 92 **U** 238.0 uranium
- 93 **Np** [237] neptunium
- 94 **Pu** [244] plutonium
- 95 **Am** [243] americium
- 96 **Cm** [247] curium
- 97 **Bk** [247] berkelium
- 98 **Cf** [251] californium
- 99 **Es** [252] einsteinium
- 100 **Fm** [257] fermium
- 101 **Md** [258] mendelevium
- 102 **No** [259] nobelium
- 103 **Lr** [262] lawrencium

Atomic number → 1

H ← Symbol

1.008 ← Atomic mass

Name → hydrogen

Color Code

Metal	**Solid**
Metalloid	**Liquid**
Nonmetal	**Gas**

Elements in the periodic table are organized according to their properties.

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); **nonmetals** (elements that appear dull, poor conductors of heat and electricity—shaded green); and **metalloids** (elements that conduct heat and electricity

moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12; and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**; [link]). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and the **noble gases** (group 18, also known as **inert gases**). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1A and group 7A elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

Periodic Table of the Elements

The periodic table organizes elements with similar properties into groups.

Note:

Click on this link for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this one that shows photos of all the elements.

Example:

Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

(a) chlorine

(b) calcium

(c) sodium

(d) sulfur

Solution

The family names are as follows:

(a) halogen

(b) alkaline earth metal

(c) alkali metal

(d) chalcogen

Check Your Learning

Give the group name for each of the following elements:

(a) krypton

(b) selenium

(c) barium

(d) lithium

Note:

Answer:

(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry

chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

Key Concepts and Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

(a) uranium

(b) bromine

(c) strontium

(d) neon

(e) gold

(f) americium

(g) rhodium

(h) sulfur

(i) carbon

(j) potassium

Solution:

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

Exercise:

Problem:

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

(a) cobalt

(b) europium

(c) iodine

(d) indium

(e) lithium

(f) oxygen

(h) cadmium

(i) terbium

(j) rhenium

Exercise:

Problem:

Using the periodic table, identify the lightest member of each of the following groups:

(a) noble gases

(b) alkaline earth metals

(c) alkali metals

(d) chalcogens

Solution:

(a) He; (b) Be; (c) Li; (d) O

Exercise:

Problem:

Using the periodic table, identify the heaviest member of each of the following groups:

(a) alkali metals

(b) chalcogens

(c) noble gases

(d) alkaline earth metals

Exercise:

Problem:

Use the periodic table to give the name and symbol for each of the following elements:

(a) the noble gas in the same period as germanium

(b) the alkaline earth metal in the same period as selenium

(c) the halogen in the same period as lithium

(d) the chalcogen in the same period as cadmium

Solution:

(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

Exercise:

Problem:

Use the periodic table to give the name and symbol for each of the following elements:

(a) the halogen in the same period as the alkali metal with 11 protons

(b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons

(c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons

(d) the noble gas in the same period as gold

Exercise:

Problem:

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

(a) the alkali metal with 11 protons and a mass number of 23

(b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom

(c) the isotope with 33 protons and 40 neutrons in its nucleus

(d) the alkaline earth metal with 88 electrons and 138 neutrons

Solution:

(a) $^{23}_{11}\text{Na}$; (b) $^{129}_{54}\text{Xe}$; (c) $^{73}_{33}\text{As}$; (d) $^{226}_{88}\text{Ra}$

Exercise:

Problem:

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

(a) the chalcogen with a mass number of 125

(b) the halogen whose longest-lived isotope is radioactive

(c) the noble gas, used in lighting, with 10 electrons and 10 neutrons

(d) the lightest alkali metal with three neutrons

Glossary

actinide
    inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal
    element in group 1

alkaline earth metal
    element in group 2

chalcogen
     element in group 16

group
     vertical column of the periodic table

halogen
     element in group 17

inert gas
     (also, noble gas) element in group 18

inner transition metal
     (also, lanthanide or actinide) element in the bottom two rows; if in the
     first row, also called lanthanide, or if in the second row, also called
     actinide

lanthanide
     inner transition metal in the top of the bottom two rows of the periodic
     table

main-group element
     (also, representative element) element in columns 1, 2, and 12–18

metal
     element that is shiny, malleable, good conductor of heat and electricity

metalloid
     element that conducts heat and electricity moderately well, and
     possesses some properties of metals and some properties of nonmetals

noble gas
     (also, inert gas) element in group 18

nonmetal
     element that appears dull, poor conductor of heat and electricity

period
     (also, series) horizontal row of the periodic table

periodic law
    properties of the elements are periodic function of their atomic numbers.

periodic table
    table of the elements that places elements with similar chemical properties close together

pnictogen
    element in group 15

representative element
    (also, main-group element) element in columns 1, 2, and 12–18

series
    (also, period) horizontal row of the period table

transition metal
    element in columns 3–11

Introduction
class="introduction"

- Nuclear Structure and Stability
- Nuclear Equations
- Radioactive Decay
- Transmutation and Nuclear Energy
- Uses of Radioisotopes
- Biological Effects of Radiation

Nuclear chemistry provides the basis for many useful diagnostic and therapeutic methods in medicine, such as these positron emission tomography (PET) scans. The PET/computed tomography scan on the left shows muscle activity. The brain scans in the center show chemical differences in

dopamine signaling in the brains of addicts and nonaddicts. The images on the right show an oncological application of PET scans to identify lymph node metastasis.
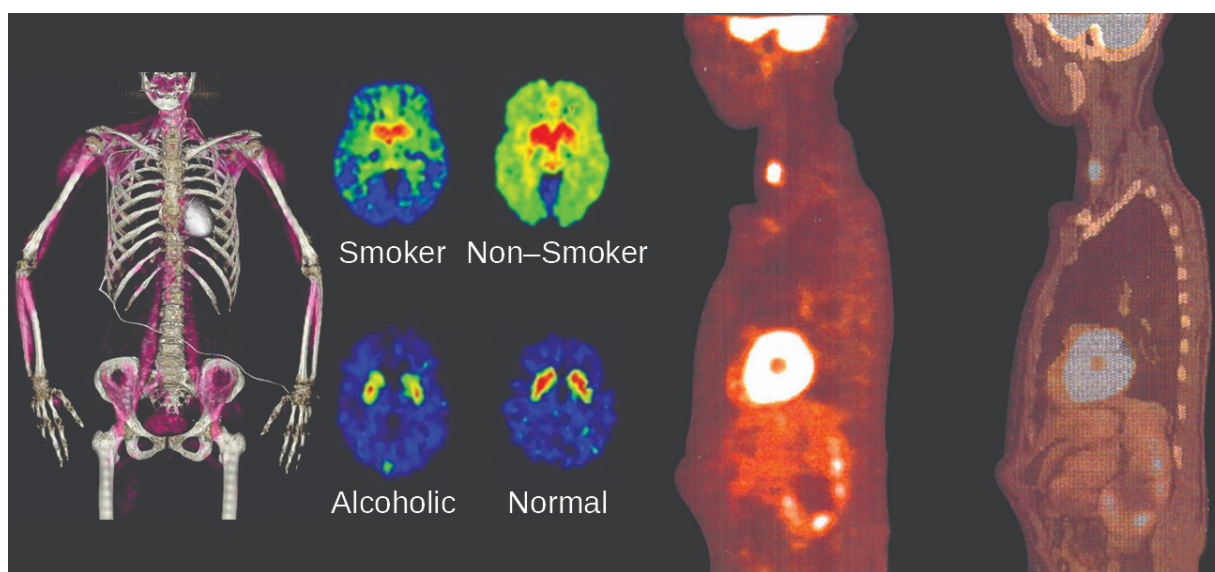
The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the electrons around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions.

This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and

twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

Nuclear Structure and Stability
By the end of this section, you will be able to:

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of $_1^1\text{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation $_Z^A\text{X}$, where X is the symbol for the element, A is the mass number, and Z is the atomic number (for example, $_6^{14}\text{C}$). Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $_6^{14}\text{C}$ is called "carbon-14."

Protons and neutrons, collectively called **nucleons**, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger).

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the **strong nuclear force**. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:
Equation:

$$\underset{\text{protons}}{(2 \times 1.0073 \text{ amu})} + \underset{\text{neutrons}}{(2 \times 1.0087 \text{ amu})} + \underset{\text{electrons}}{(2 \times 0.00055 \text{ amu})} = 4.0331 \text{ amu}$$

However, mass spectrometric measurements reveal that the mass of an $_2^4\text{He}$ atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the **mass defect** of the atom. In the case of helium, the mass defect indicates a "loss" in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The **nuclear binding energy** is the energy produced when the atoms' nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the **mass-energy equivalence equation** as stated by Albert Einstein:
**Equation:**

$$E = mc^2$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its mass defect. A variety of units are commonly used for nuclear binding energies, including **electron volts (eV)**, with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making 1 eV = 1.602×10^{-19} J.

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the **band of stability** (also called the belt, zone, or valley of stability). The straight line in [link] represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.
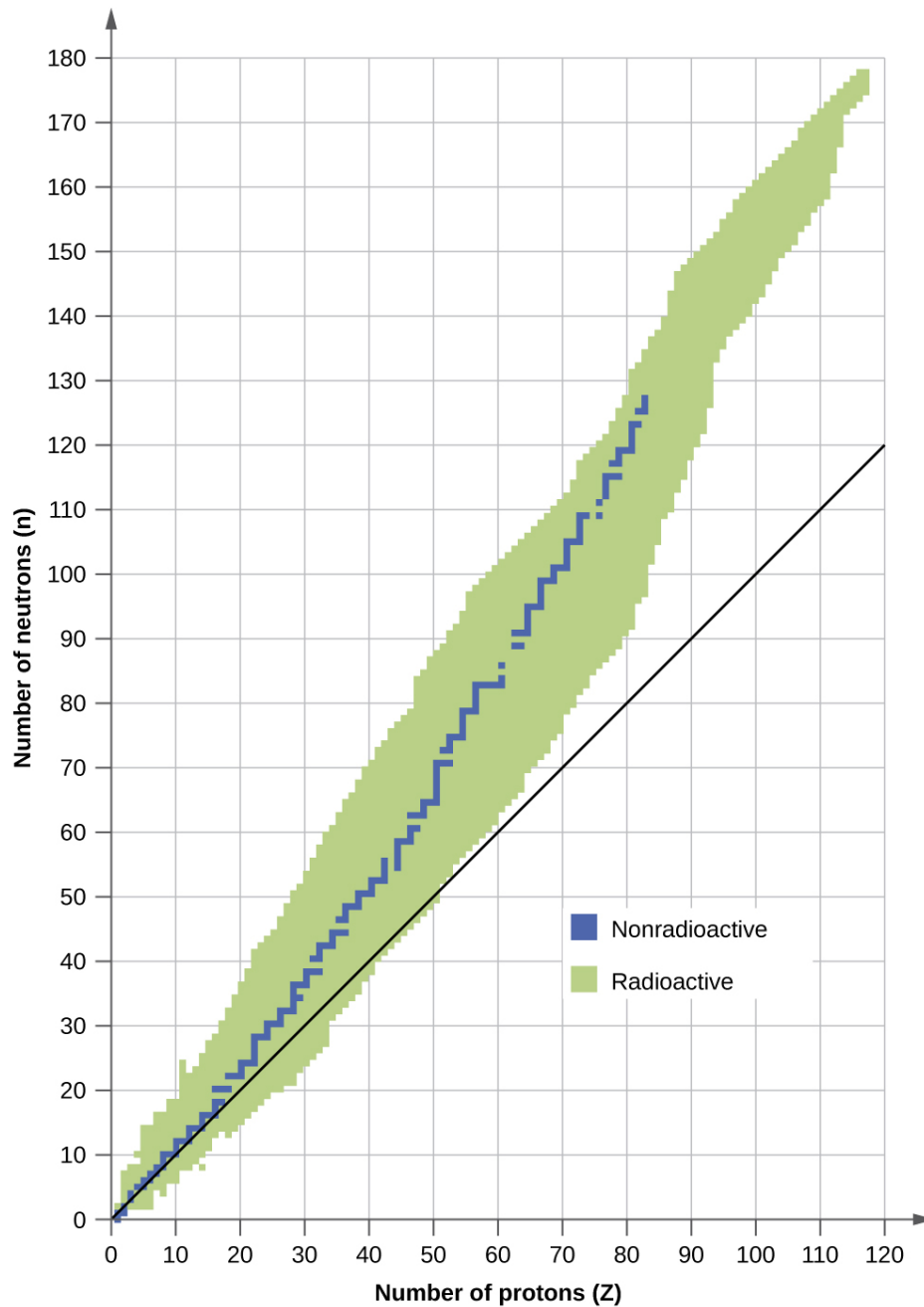
This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit **radioactivity**. They change spontaneously (decay) into other nuclei that are

either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or **radioisotope**) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (see [link]). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as $_2^4\text{He}$, $_8^{16}\text{O}$, $_{20}^{40}\text{Ca}$, and $_{82}^{208}\text{Pb}$, are called "double magic" and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Stable Nuclear Isotopes		
Number of Stable Isotopes	**Proton Number**	**Neutron Number**
157	even	even
53	even	odd
50	odd	even
5	odd	odd

The relative stability of a nucleus is correlated with its **binding energy per nucleon**, the total binding energy for the nucleus divided by the number or nucleons in the nucleus.
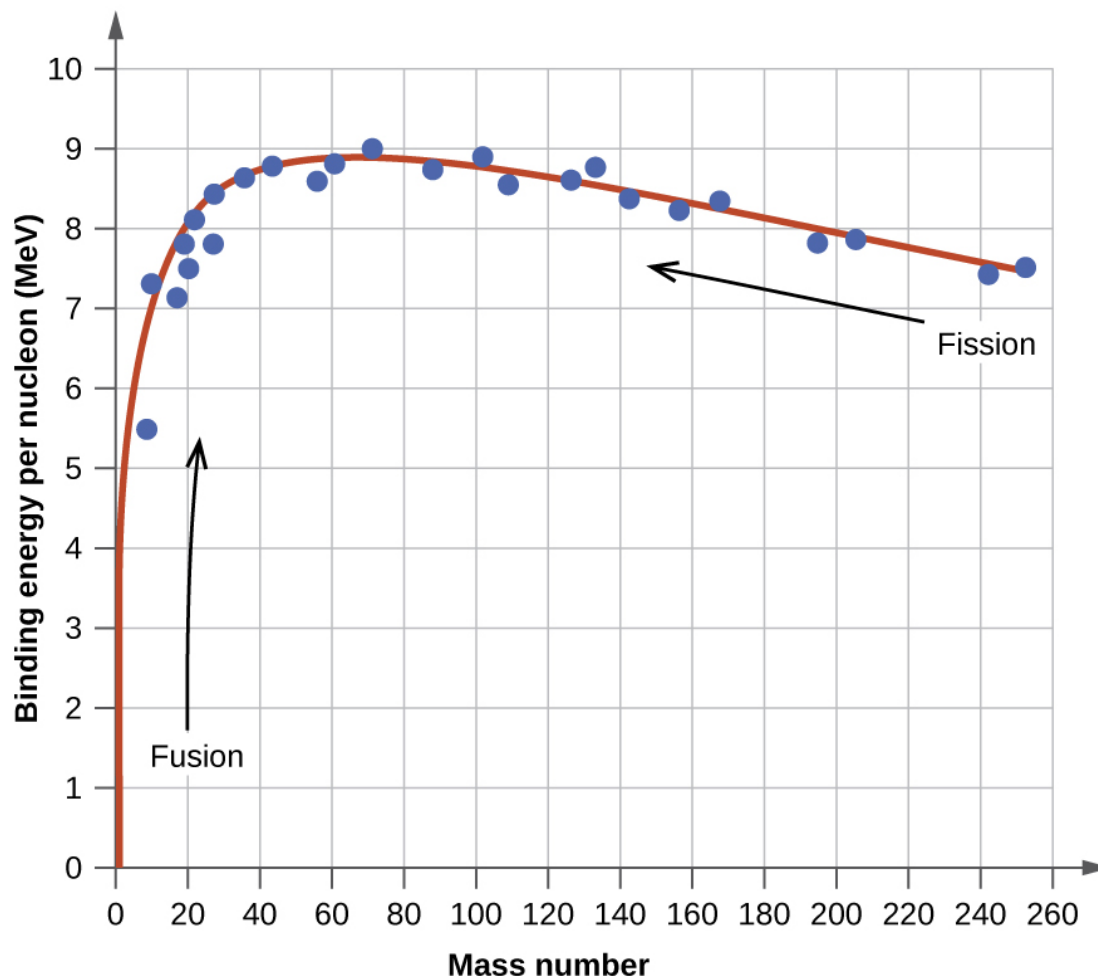
The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

Key Concepts and Summary

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This "missing" mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein's mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus

number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

Key Equations

- $E = mc^2$

Chemistry End of Chapter Exercises

Exercise:

Problem: Write the following isotopes in hyphenated form (e.g., "carbon-14")

(a) $^{24}_{11}Na$

(b) $^{29}_{13}Al$

(c) $^{73}_{36}Kr$

(d) $^{194}_{77}Ir$
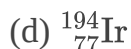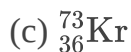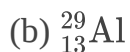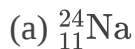
Solution:

(a) sodium-24; (b) aluminum-29; (c) krypton-73; (d) iridium-194

Exercise:

Problem: Write the following isotopes in nuclide notation (e.g., "$^{14}_{6}C$")

(a) oxygen-14

(b) copper-70

(c) tantalum-175

(d) francium-217

Exercise:

Problem:

For the following isotopes that have missing information, fill in the missing information to complete the notation

(a) $^{34}_{14}X$

(b) $^{36}_{X}P$

(c) $^{57}_{X}Mn$

(d) $^{121}_{56}X$

Solution:

(a) $^{34}_{14}Si$; (b) $^{36}_{15}P$; (c) $^{57}_{25}Mn$; (d) $^{121}_{56}Ba$
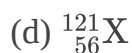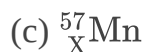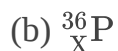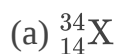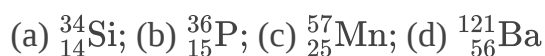
Exercise:

Problem:

For each of the isotopes in [link], determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

Exercise:

Problem:

Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

(a) 25 protons, 20 neutrons, 24 electrons

(b) 45 protons, 24 neutrons, 43 electrons

(c) 53 protons, 89 neutrons, 54 electrons

(d) 97 protons, 146 neutrons, 97 electrons

Solution:

(a) $^{45}_{25}Mn^{+1}$; (b) $^{69}_{45}Rh^{+2}$; (c) $^{142}_{53}I^{-1}$; (d) $^{243}_{97}Bk$
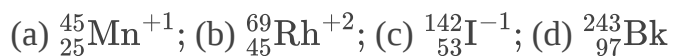
Exercise:

Problem:

What are the two principal differences between nuclear reactions and ordinary chemical changes?

Solution:

Nuclear reactions usually change one type of nucleus into another; chemical changes rearrange atoms. Nuclear reactions involve much larger energies than chemical reactions and have measureable mass changes.

Exercise:

Problem:

Which of the following nuclei lie within the band of stability shown in [link]?

(a) chlorine-37

(b) calcium-40

(c) ^{204}Bi

(d) ^{56}Fe

(e) ^{206}Pb

(f) ^{211}Pb

(g) ^{222}Rn

(h) carbon-14

Solution:

(a), (b), (c), (d), and (e)

Exercise:

Problem:

Which of the following nuclei lie within the band of stability shown in [link]?

(a) argon-40

(b) oxygen-16

(c) ^{122}Ba

(d) ^{58}Ni

(e) ^{205}Tl

(f) ^{210}Tl

(g) ^{226}Ra

(h) magnesium-24

Glossary

band of stability
 (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

binding energy per nucleon
 total binding energy for the nucleus divided by the number of nucleons in the nucleus

electron volt (eV)
 measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

magic number
 nuclei with specific numbers of nucleons that are within the band of stability

mass defect
 difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass "lost" when nucleons are brought together to form a nucleus)

mass-energy equivalence equation
 Albert Einstein's relationship showing that mass and energy are equivalent

nuclear binding energy
 energy lost when an atom's nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry
 study of the structure of atomic nuclei and processes that change nuclear structure

nucleon
 collective term for protons and neutrons in a nucleus

nuclide
 nucleus of a particular isotope

radioactivity

    phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radioisotope

    isotope that is unstable and undergoes conversion into a different, more stable isotope

strong nuclear force

    force of attraction between nucleons that holds a nucleus together

Nuclear Equations
By the end of this section, you will be able to:

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are **nuclear reactions**. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in [link]. Protons $\left({}_{1}^{1}p, \right.$ also represented by the symbol ${}_{1}^{1}H \left. \right)$ and neutrons $\left({}_{0}^{1}n \right)$ are the constituents of atomic nuclei, and have been described previously. **Alpha particles** $\left({}_{2}^{4}He, \right.$ also represented by the symbol ${}_{2}^{4}\alpha \left. \right)$ are high-energy helium nuclei. **Beta particles** $\left({}_{-1}^{0}\beta, \right.$ also represented by the symbol ${}_{-1}^{0}e \left. \right)$ are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. **Positrons** $\left({}_{+1}^{0}e, \right.$ also represented by the symbol ${}_{+1}^{0}\beta \left. \right)$ are positively charged electrons ("anti-electrons"). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized ${}_{2}^{4}He$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Name	Symbol(s)	Representation	Description
Alpha particle	$^{4}_{2}\text{He}$ or $^{4}_{2}\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$^{0}_{1}\text{e}$ or $^{0}_{-1}\beta$		(High-energy) electrons
Positron	$^{0}_{+1}\text{e}$ or $^{0}_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	$^{1}_{1}\text{H}$ or $^{1}_{1}\text{p}$		Nuclei of hydrogen atoms
Neutron	$^{1}_{0}\text{n}$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ	γ	Very high-energy electromagnetic radiation

Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of **antimatter**, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of **gamma rays (γ)**—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

Equation:

$$^{0}_{-1}\text{e} + {}^{0}_{+1}\text{e} \longrightarrow \gamma + \gamma$$
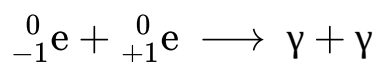
As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}\text{O}$ is a product of the nuclear reaction of $^{14}_{7}\text{N}$ and $^{4}_{2}\text{He}$ if we knew that a proton, $^{1}_{1}\text{H}$, was one of the two products. [link] shows how we can identify a nuclide by balancing the nuclear reaction.

Example:
Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 $\left(^{25}_{12}\text{Mg}\right)$ produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

Equation:

$$^{25}_{12}\text{Mg} + {}^{4}_{2}\text{He} \longrightarrow {}^{1}_{1}\text{H} + {}^{A}_{Z}\text{X}$$
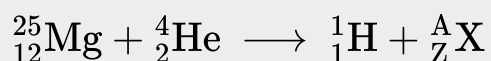
where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

Equation:

$$25 + 4 = A + 1, \text{ or } A = 28$$

Similarly, the charges must balance, so:

Equation:

$$12 + 2 = Z + 1, \text{ and } Z = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\text{Al}$.

Check Your Learning

The nuclide $^{125}_{53}\text{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Note:

Answer:

$^{125}_{53}\text{I} + {}^{0}_{-1}\text{e} \longrightarrow {}^{125}_{52}\text{Te}$
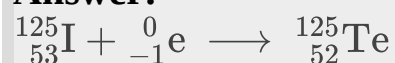
Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:
  Equation:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$
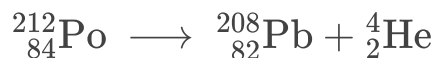
- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:
  Equation:

$$^{14}_{7}\text{N} + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$
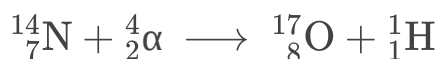
- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:
  Equation:

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$
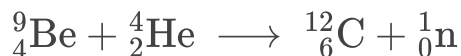
- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:
  Equation:

$$^{2}_{1}\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^{1}_{0}\text{n} + {}^{97}_{43}\text{Tc}$$
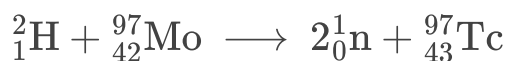
- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:
  Equation:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^{1}_{0}\text{n}$$

Key Concepts and Summary

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Write a brief description or definition of each of the following:

(a) nucleon

(b) α particle

(c) β particle

(d) positron

(e) γ ray

(f) nuclide

(g) mass number

(h) atomic number

Solution:

(a) A nucleon is any particle contained in the nucleus of the atom, so it can refer to protons and neutrons. (b) An α particle is one product of natural radioactivity and is the nucleus of a helium atom. (c) A β particle is a product of natural radioactivity and is a high-speed electron. (d) A positron is a particle with the same mass as an electron but with a positive charge. (e) Gamma rays compose electromagnetic radiation of high energy and short wavelength. (f) Nuclide is a term used when referring to a single type of nucleus. (g) The mass number is the sum of the number of protons and the number of neutrons in an element. (h) The atomic number is the number of protons in the nucleus of an element.

Exercise:

Problem:

Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

Exercise:

Problem:

Complete each of the following equations by adding the missing species:
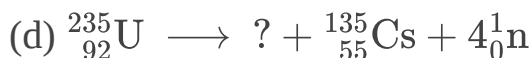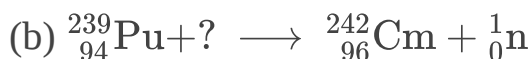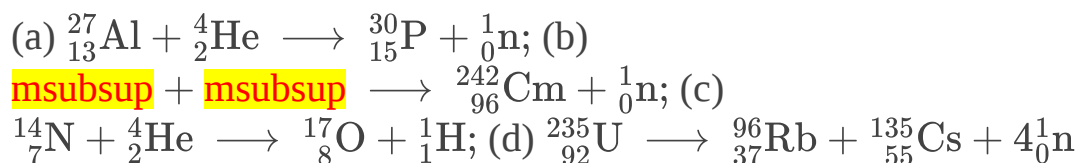
(a) $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow ?\ + ^{1}_{0}\text{n}$

(b) $^{239}_{94}\text{Pu} + ? \longrightarrow ^{242}_{96}\text{Cm} + ^{1}_{0}\text{n}$

(c) $^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow ?\ + ^{1}_{1}\text{H}$

(d) $^{235}_{92}\text{U} \longrightarrow ?\ + ^{135}_{55}\text{Cs} + 4^{1}_{0}\text{n}$

Solution:

(a) $^{27}_{13}\text{Al} + ^4_2\text{He} \longrightarrow ^{30}_{15}\text{P} + ^1_0\text{n}$; (b)
<mark>msubsup</mark> + <mark>msubsup</mark> $\longrightarrow ^{242}_{96}\text{Cm} + ^1_0\text{n}$; (c)
$^{14}_7\text{N} + ^4_2\text{He} \longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$; (d) $^{235}_{92}\text{U} \longrightarrow ^{96}_{37}\text{Rb} + ^{135}_{55}\text{Cs} + 4^1_0\text{n}$

Exercise:

Problem: Complete each of the following equations:

(a) $^7_3\text{Li} + ? \longrightarrow 2^4_2\text{He}$

(b) $^{14}_6\text{C} \longrightarrow ^{14}_7\text{N} + ?$

(c) $^{27}_{13}\text{Al} + ^4_2\text{He} \longrightarrow ? + ^1_0\text{n}$

(d) $^{250}_{96}\text{Cm} \longrightarrow ? + ^{98}_{38}\text{Sr} + 4^1_0\text{n}$
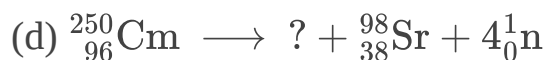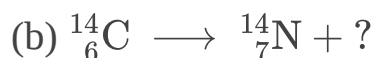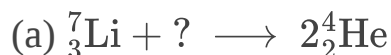
Exercise:

Problem:

Write a balanced equation for each of the following nuclear reactions:

(a) the production of ^{17}O from ^{14}N by α particle bombardment

(b) the production of ^{14}C from ^{14}N by neutron bombardment

(c) the production of ^{233}Th from ^{232}Th by neutron bombardment

(d) the production of ^{239}U from ^{238}U by ^2_1H bombardment

Solution:

(a) $^{14}_7\text{N} + $ <mark>msubsup</mark> $\longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$; (b) $^{14}_7\text{N} + ^1_0\text{n} \longrightarrow ^{14}_6\text{N} + ^1_1\text{H}$;
(c) $^{232}_{90}\text{Th} + ^1_0\text{n} \longrightarrow ^{233}_{90}\text{Th}$; (d) $^{238}_{92}\text{U} + ^2_1\text{H} \longrightarrow ^{239}_{92}\text{U} + ^1_1\text{H}$
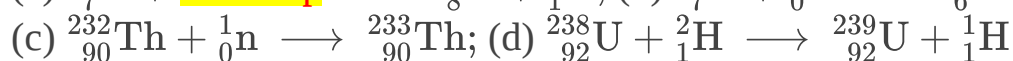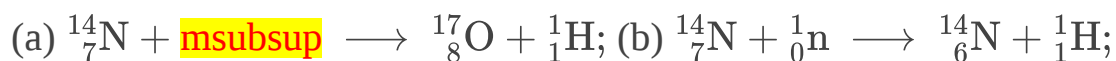
Exercise:

Problem:

Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as ^{99}Tc*. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

Glossary

alpha particle
    $\left(\alpha \text{ or } {}^{4}_{2}\mathbf{He} \text{ or } {}^{4}_{2}\alpha\right)$ high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

antimatter
    particles with the same mass but opposite properties (such as charge) of ordinary particles

beta particle
    $\left(\beta \text{ or } {}^{0}_{-1}\mathbf{e} \text{ or } {}^{0}_{-1}\beta\right)$ high-energy electron

gamma ray
    $\left(\gamma \text{ or } {}^{0}_{0}\gamma\right)$ short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

nuclear reaction
    change to a nucleus resulting in changes in the atomic number, mass number, or energy state

positron $\left({}^{0}_{+1}\beta \text{ or } {}^{0}_{+1}\mathbf{e}\right)$
    antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

Radioactive Decay
By the end of this section, you will be able to:

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term "radioactivity," and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is **radioactive decay**. The unstable nuclide is called the **parent nuclide**; the nuclide that results from the decay is known as the **daughter nuclide**. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo ([link]).
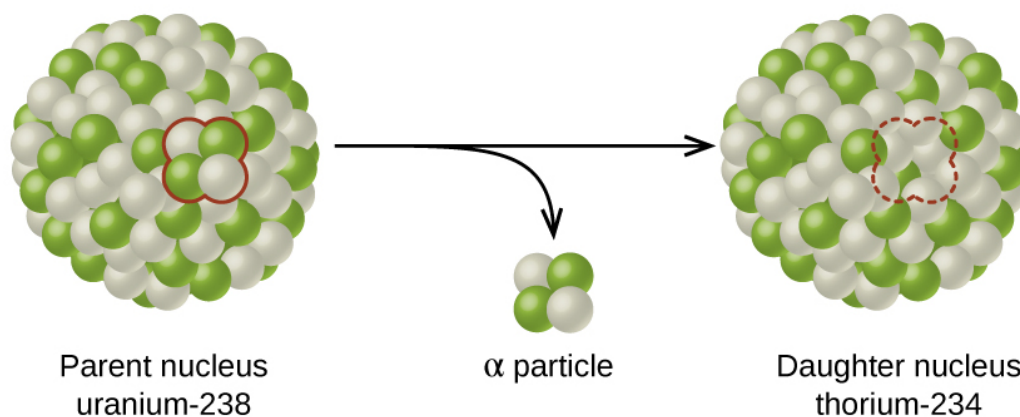
A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

Note:

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field ([link]) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.
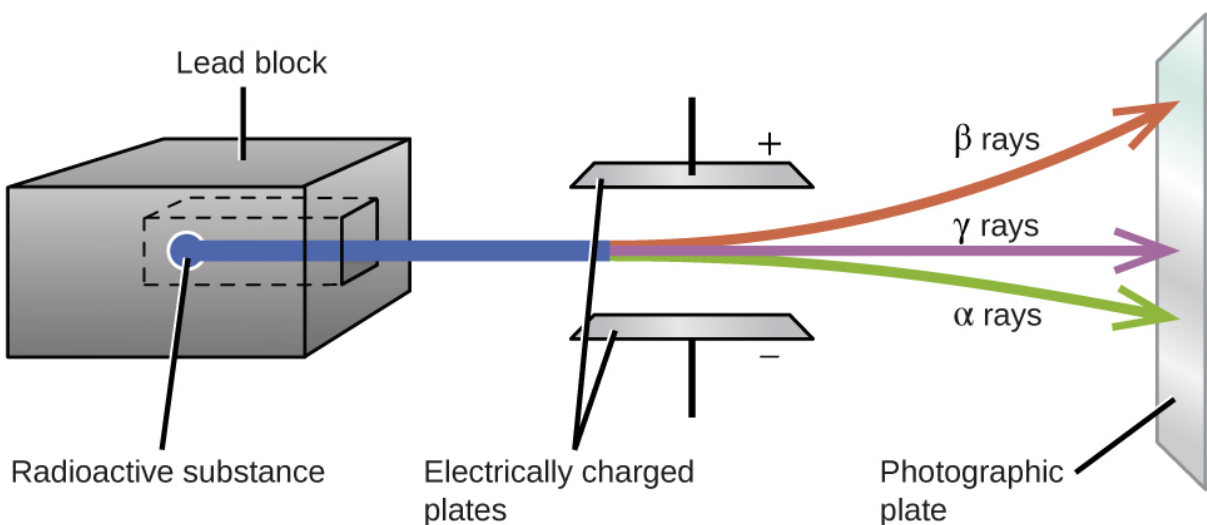
Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:
Equation:

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{206}_{82}\text{Pb} \qquad \text{or} \qquad {}^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\alpha + {}^{206}_{82}\text{Pb}$$
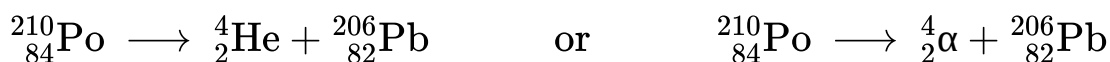
Alpha decay occurs primarily in heavy nuclei (A > 200, Z > 83). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below the band of stability (refer to [link]), the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:
Equation:

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\text{e} + {}^{131}_{54}\text{X} \qquad \text{or} \qquad {}^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\text{Xe}$$
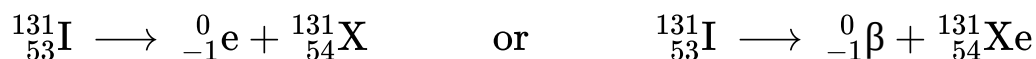
Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:
Equation:

$$^{60}_{27}\text{Co}^{*} \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{27}\text{Co}$$
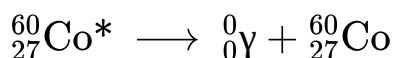
There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β$^+$ decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:
Equation:

$$^{15}_{8}O \longrightarrow {}^{0}_{+1}e + {}^{15}_{7}N \qquad \text{or} \qquad {}^{15}_{8}O \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}N$$
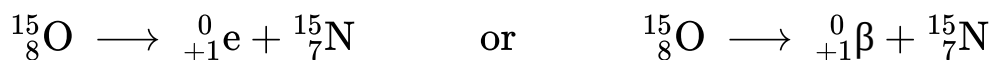
Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:
Equation:

$$^{40}_{19}K + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}Ar$$
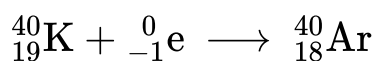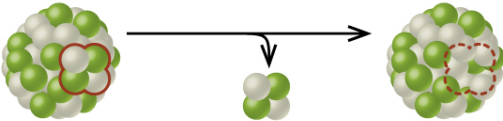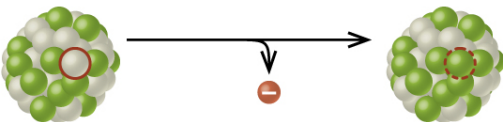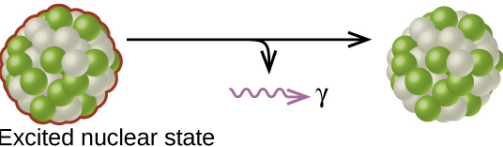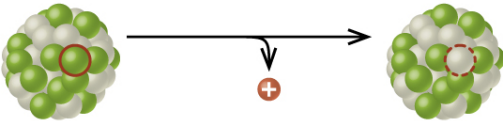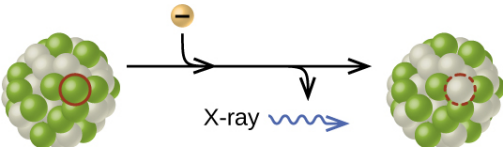
Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict.

The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

[link] summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$^A_Z X \longrightarrow \, ^4_2 He + \, ^{A-4}_{Z-2} Y$		A: decrease by 4 Z: decrease by 2
Beta decay	$^A_Z X \longrightarrow \, ^0_{-1} e + \, ^A_{Z+1} Y$		A: unchanged Z: increase by 1
Gamma decay	$^A_Z X \longrightarrow \, ^0_0 \gamma + \, ^A_Z Y$	Excited nuclear state	A: unchanged Z: unchanged
Positron emission	$^A_Z X \longrightarrow \, ^0_{+1} e + \, ^A_{Y-1} Y$		A: unchanged Z: decrease by 1
Electron capture	$^A_Z X \longrightarrow \, ^0_{-1} e + \, ^A_{Y-1} Y$	X-ray	A: unchanged Z: decrease by 1

This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

Note:
PET Scan
Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how

parts of a patient's body function ([link]). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This "tagged" compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.
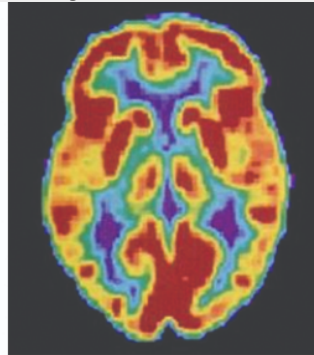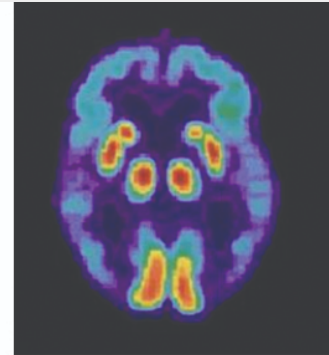
(a)   (b)   (c)

A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

For example, F-18 is produced by proton bombardment of ^{18}O $\left(^{18}_{8}\text{O} + {}^{1}_{1}\text{p} \longrightarrow {}^{18}_{9}\text{F} + {}^{1}_{0}\text{n}\right)$ and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike

magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or **radioactive decay series**. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability ([link]). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.
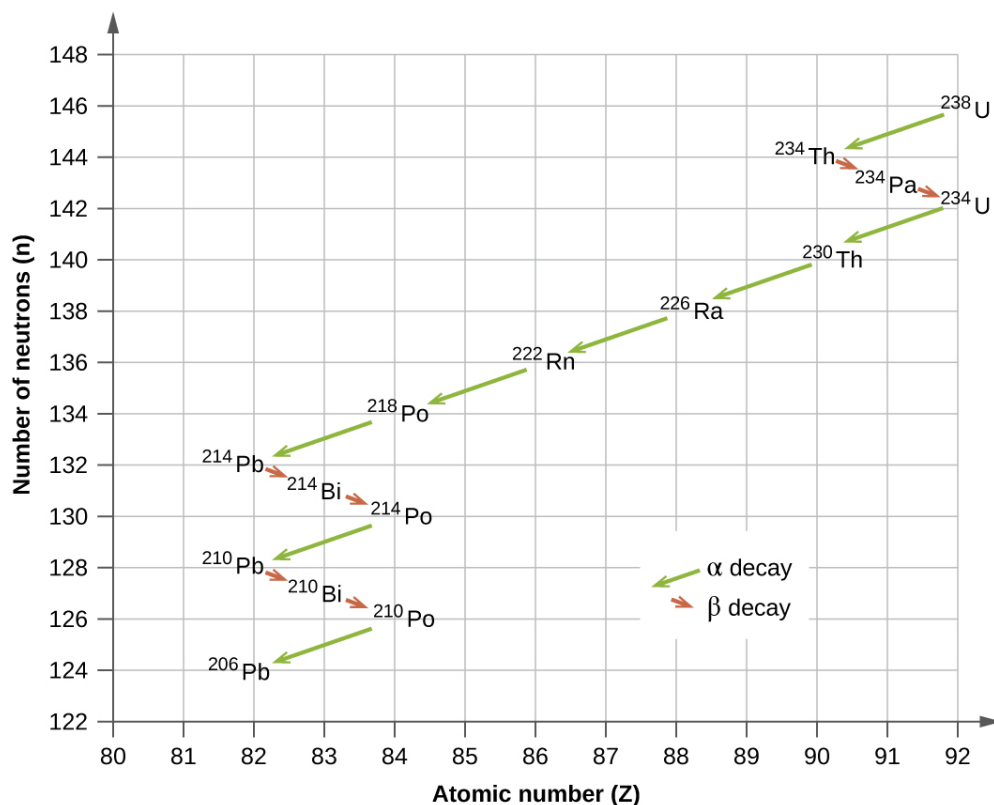
Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years ([link]). In a given cobalt-60 source, since half of the $^{60}_{27}Co$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.
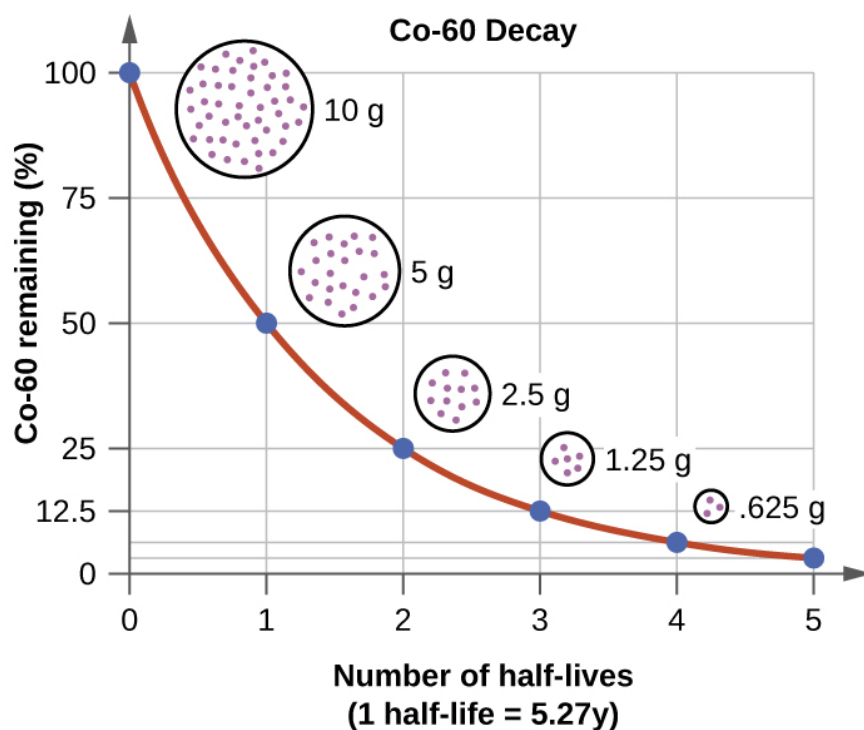
For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-

lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\text{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\text{Ra}$ is 24,000 years; $^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in [link], and others are listed in Appendix M.

Half-lives of Radioactive Isotopes Important to Medicine			
Type[footnote] The "m" in Tc-99m stands for "metastable," indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.	**Decay Mode**	**Half-Life**	**Uses**
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone

I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}C$, which constitutes about 99% of the carbon on earth; $^{13}_{6}C$, about 1% of the total;

and trace amounts of $^{14}_{6}C$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:
Equation:

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$
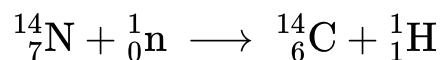
All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}CO_2$ to $^{12}_{6}CO_2$ depends on the ratio of $^{14}_{6}CO$ to $^{12}_{6}CO$ in the atmosphere. The natural abundance of $^{14}_{6}CO$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}C^{14}_{6}CO_2$ and $^{12}_{6}CO_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}C$: $^{12}_{6}C$ ratio found in a living plant is the same as the $^{14}_{6}C$: $^{12}_{6}C$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}C$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:
Equation:

$$^{14}_{6}C \longrightarrow ^{12}_{7}N + ^{0}_{-1}e$$
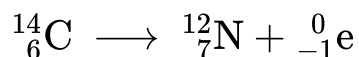
Thus, the $^{14}_{6}C$: $^{12}_{6}C$ ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). [link] visually depicts this process.
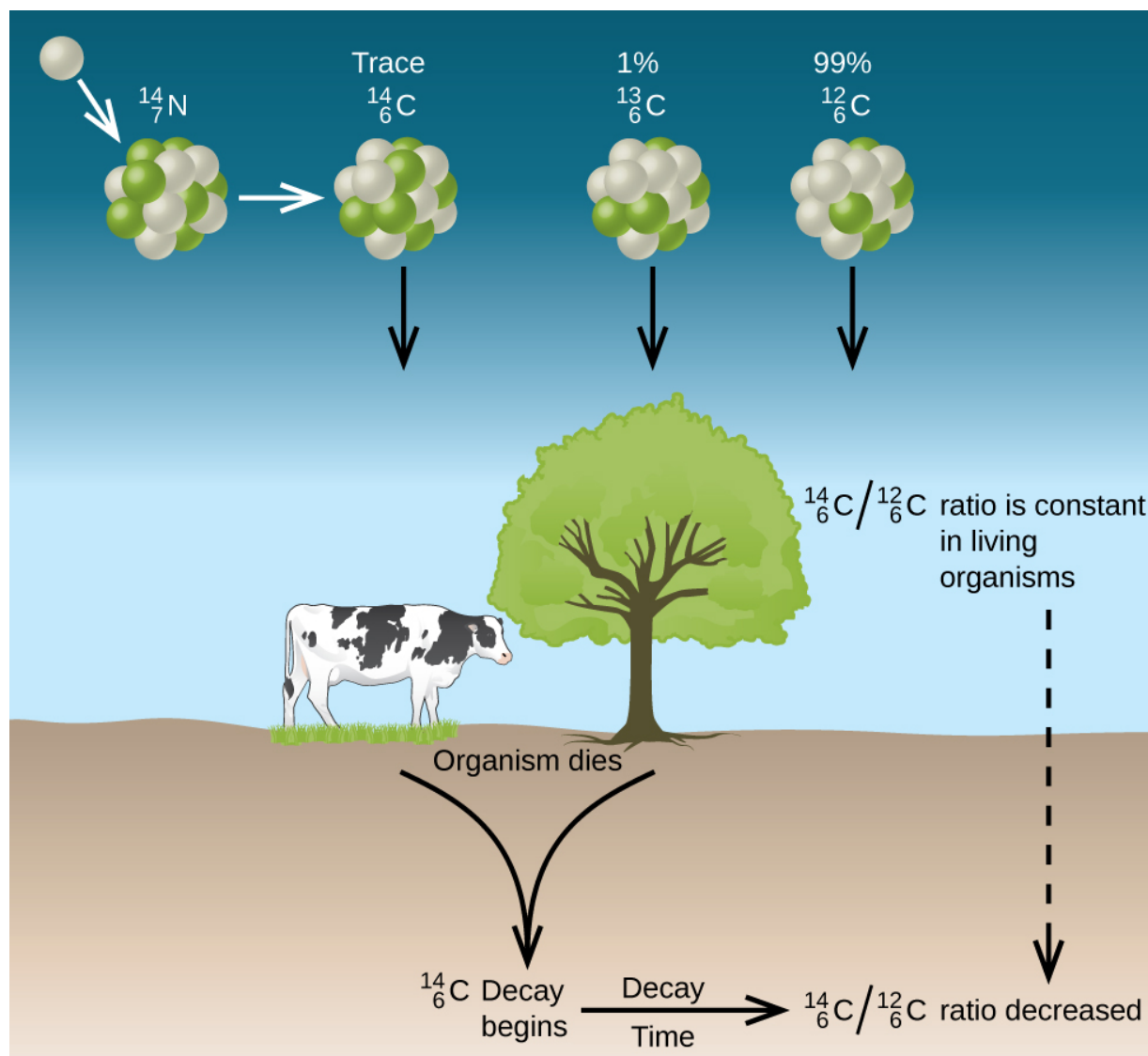
Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of $^{14}_{6}\text{C}$ being 5730 years, if the $^{14}_{6}\text{C}$: $^{12}_{6}\text{C}$ ratio in a wooden object found in an archaeological dig is half what it is in a

living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of $_6^{14}C$: $_6^{12}C$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

There have been some significant, well-documented changes to the $_6^{14}C$: $_6^{12}C$ ratio. The accuracy of a straightforward application of this technique depends on the $_6^{14}C$: $_6^{12}C$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely $_6^{12}CO_2$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the $_6^{14}C$ has decayed), the ratio of $_6^{14}C$: $_6^{12}C$ in the atmosphere may be changing. This manmade increase in $_6^{12}CO_2$ in the atmosphere causes the $_6^{14}C$: $_6^{12}C$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Key Concepts and Summary

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is

a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

Key Equations

- decay rate $= \lambda N$
- $t_{1/2} = \dfrac{\ln 2}{\lambda} = \dfrac{0.693}{\lambda}$

Chemistry End of Chapter Exercises

Exercise:

Problem:

What are the types of radiation emitted by the nuclei of radioactive elements?

Solution:

α (helium nuclei), β (electrons), β^+ (positrons), and η (neutrons) may be emitted from a radioactive element, all of which are particles; γ rays also may be emitted.

Exercise:

Problem:

What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

(a) an α particle is emitted

(b) a β particle is emitted

(c) γ radiation is emitted

(d) a positron is emitted

(e) an electron is captured

Exercise:

Problem:

What is the change in the nucleus that results from the following decay scenarios?

(a) emission of a β particle

(b) emission of a β$^+$ particle

(c) capture of an electron

Solution:

(a) conversion of a neutron to a proton: $^1_0 n \longrightarrow \, ^1_1 p + \, ^0_{+1} e$; (b) conversion of a proton to a neutron; the positron has the same mass as an electron and the same magnitude of positive charge as the electron has negative charge; when the n:p ratio of a nucleus is too low, a proton is converted into a neutron with the emission of a positron: $^1_1 p \longrightarrow \, ^1_0 n + \, ^0_{+1} e$; (c) In a proton-rich nucleus, an inner atomic electron can be absorbed. In simplest form, this changes a proton into a neutron: $^1_1 p + \, ^0_{-1} e \longrightarrow \, ^1_0 p$

Exercise:

Problem:

Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

Exercise:

Problem:

Why is electron capture accompanied by the emission of an X-ray?

Solution:

The electron pulled into the nucleus was most likely found in the 1*s* orbital. As an electron falls from a higher energy level to replace it, the difference in the energy of the replacement electron in its two energy levels is given off as an X-ray.

Exercise:

Problem:

Explain, in terms of [link], how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

Exercise:

Problem:

Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

(a) chromium-53

(b) manganese-51

(c) iron-59

Solution:

Manganese-51 is most likely to decay by positron emission. The n:p ratio for Cr-53 is $\frac{29}{24}$ = 1.21; for Mn-51, it is $\frac{26}{25}$ = 1.04; for Fe-59, it is $\frac{33}{26}$ = 1.27. Positron decay occurs when the n:p ratio is low. Mn-51 has the lowest n:p ratio and therefore is most likely to decay by positron emission. Besides, $^{53}_{24}Cr$ is a stable isotope, and $^{59}_{26}Fe$ decays by beta emission.

Exercise:

Problem:

Write a nuclear reaction for each step in the formation of $^{218}_{84}\text{Po}$ from $^{238}_{98}\text{U}$, which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α particles, in that order.

Solution:

$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}; \, {}^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}\text{e};$
$^{234}_{91}\text{Pa} \longrightarrow {}^{234}_{92}\text{U} + {}^{0}_{-1}\text{e}; \, {}^{234}_{92}\text{U} \longrightarrow {}^{230}_{90}\text{Th} + {}^{4}_{2}\text{He}$
$^{230}_{90}\text{Th} \longrightarrow {}^{226}_{88}\text{Ra} + {}^{4}_{2}\text{He} \, {}^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He};$
$^{222}_{86}\text{Rn} \longrightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$
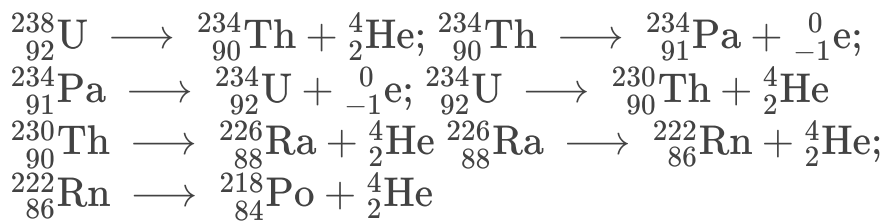
Exercise:

Problem:

Write a nuclear reaction for each step in the formation of $^{208}_{82}\text{Pb}$ from $^{228}_{90}\text{Th}$, which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

Exercise:

Problem: Define the term half-life and illustrate it with an example.

Solution:

Half-life is the time required for half the atoms in a sample to decay. Example (answers may vary): For C-14, the half-life is 5770 years. A 10-g sample of C-14 would contain 5 g of C-14 after 5770 years; a 0.20-g sample of C-14 would contain 0.10 g after 5770 years.

Exercise:

Problem:

Write a balanced equation for each of the following nuclear reactions:

(a) bismuth-212 decays into polonium-212

(b) beryllium-8 and a positron are produced by the decay of an unstable nucleus

(c) neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239

(d) strontium-90 decays into yttrium-90

Solution:

(a) $^{212}_{83}\text{Bi} \longrightarrow ^{212}_{84}\text{Po} + ^{0}_{-1}\text{e}$; (b) $^{8}_{5}\text{B} \longrightarrow ^{8}_{4}\text{Be} + ^{0}_{-1}\text{e}$; (c) $^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{Np}$, $^{239}_{93}\text{Np} \longrightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\text{e}$; (d) $^{90}_{38}\text{Sr} \longrightarrow ^{90}_{39}\text{Y} + ^{0}_{-1}\text{e}$
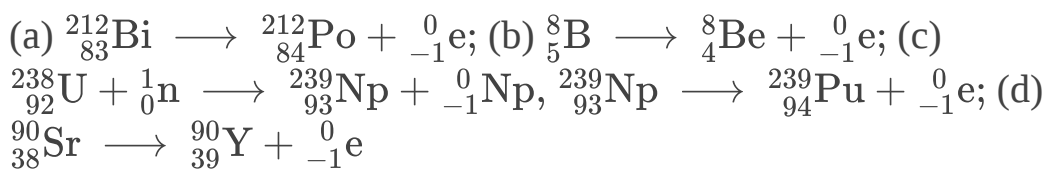
Exercise:

Problem:

Write a balanced equation for each of the following nuclear reactions:

(a) mercury-180 decays into platinum-176

(b) zirconium-90 and an electron are produced by the decay of an unstable nucleus

(c) thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay

(d) neon-19 decays into fluorine-19

Glossary

alpha (α) decay
    loss of an alpha particle during radioactive decay

beta (β) decay
    breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

daughter nuclide
> nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture
> combination of a core electron with a proton to yield a neutron within the nucleus

gamma (γ) emission
> decay of an excited-state nuclide accompanied by emission of a gamma ray

half-life ($t_{1/2}$)
> time required for half of the atoms in a radioactive sample to decay

parent nuclide
> unstable nuclide that changes spontaneously into another (daughter) nuclide

positron emission
> (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

radioactive decay
> spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series
> chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radiocarbon dating
> highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of $^{14}_{6}C$: $^{12}_{6}C$ in the object vs. the ratio of $^{14}_{6}C$: $^{12}_{6}C$ in the present-day atmosphere

radiometric dating

use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

Transmutation and Nuclear Energy
By the end of this section, you will be able to:

- Describe the synthesis of transuranium nuclides
- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission and fusion reactors

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a **transmutation** reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:
Equation:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$
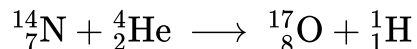
The $^{17}_{8}\text{O}$ and $^{1}_{1}\text{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

Note:

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world ([link]). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.

A small section of the LHC is shown with workers traveling along it.
(credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and

resulted in the awarding of the 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Note:

Famous physicist Brian Cox talks about his work on the Large Hadron Collider at CERN, providing an entertaining and engaging tour of this massive project and the physics behind it.
View a short video from CERN, describing the basics of how its particle accelerators work.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these— element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

Equation:

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U}$$

$$^{239}_{92}\text{U} \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e} \, t_{1/2} \qquad \text{half-life} = 23.5 \text{ min}$$

$$^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e} \, t_{1/2} \qquad \text{half-life} = 2.36 \text{ days}$$
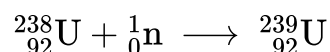
Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239,

which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

Equation:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \xrightarrow{\beta^-} ^{239}_{93}\text{Np} \xrightarrow{\beta^-} ^{239}_{94}\text{Pu}$$
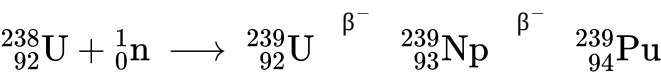
Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called **transuranium elements**. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in [link].

Preparation of Some of the Transuranium Elements			
Name	**Symbol**	**Atomic Number**	**Reaction**
americium	Am	95	$^{239}_{94}\text{Pu} + ^{1}_{0}\text{n} \longrightarrow ^{240}_{95}\text{Am} + ^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + ^{4}_{2}\text{He} \longrightarrow ^{242}_{96}\text{Cm} + ^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + ^{4}_{2}\text{He} \longrightarrow ^{243}_{97}\text{Bk} + 2^{1}_{0}\text{n}$

Preparation of Some of the Transuranium Elements			
Name	**Symbol**	**Atomic Number**	**Reaction**
einsteinium	Es	99	$^{238}_{92}U + 15^1_0n \longrightarrow \, ^{253}_{99}Es + 7^0_{-1}e$
mendelevium	Md	101	$^{253}_{99}Es + ^4_2He \longrightarrow \, ^{256}_{101}Md + ^1_0n$
nobelium	No	102	$^{246}_{96}Cm + ^{12}_6C \longrightarrow \, ^{254}_{102}No + 4^1_0n$
rutherfordium	Rf	104	$^{249}_{98}Cf + ^{12}_6C \longrightarrow \, ^{257}_{104}Rf + 4^1_0n$
seaborgium	Sg	106	$^{206}_{82}Pb + ^{54}_{24}Cr \longrightarrow \, ^{257}_{106}Sg + 3^1_0n$ $^{249}_{98}Cf + ^{18}_8O \longrightarrow \, ^{263}_{106}Sg + 4^1_0n$
meitnerium	Mt	107	$^{209}_{83}Bi + ^{58}_{26}Fe \longrightarrow \, ^{266}_{109}Mt + ^1_0n$

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56 (see [link]). Sometimes neutrons are also produced. This decomposition is called **fission**, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in [link].

$$^{235}_{92}U + ^{0}_{1}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{36}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$$
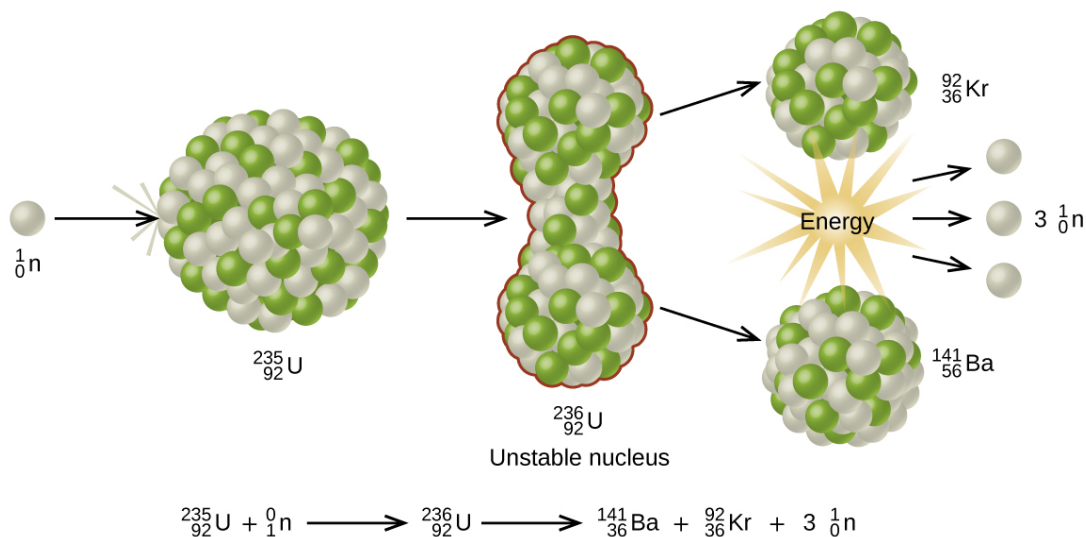
When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in [link]. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{90}_{38}Sr + {}^{144}_{54}Xe + 2\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{96}_{37}Rb + {}^{137}_{55}Cs + 3\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{137}_{52}Te + {}^{97}_{40}Zr + 2\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$$
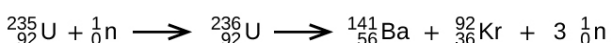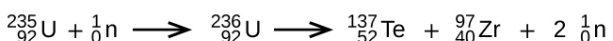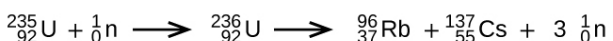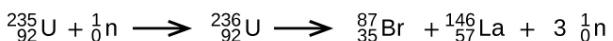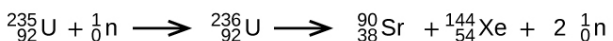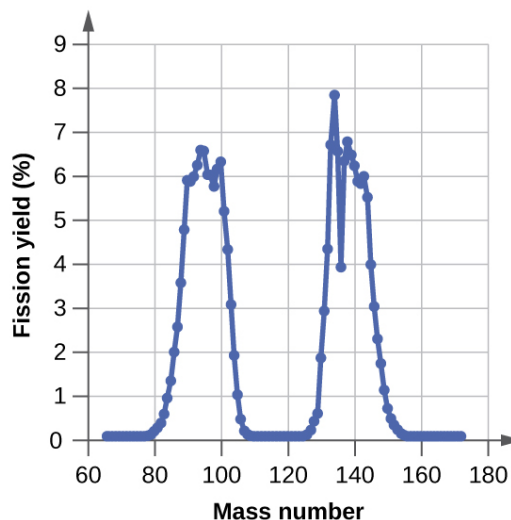
(a)   (b)

(a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

Note:

View this link to see a simulation of nuclear fission.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1

kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear **chain reaction** (see [link]). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

$$^{235}_{92}U + ^{0}_{1}n \longrightarrow ^{140}_{56}Ba + ^{93}_{36}Kr + 3 \ ^{1}_{0}n$$

(a) $^{235}_{92}U + ^{0}_{1}n \longrightarrow ^{96}_{37}Rb + ^{137}_{55}Cs + 3 \ ^{1}_{0}n$

(b) $^{235}_{92}U + ^{0}_{1}n \longrightarrow ^{90}_{38}Sr + ^{144}_{54}Xe + 2 \ ^{1}_{0}n$

(c) $^{235}_{92}U + ^{0}_{1}n \longrightarrow ^{87}_{35}Br + ^{146}_{57}La + 3 \ ^{1}_{0}n$
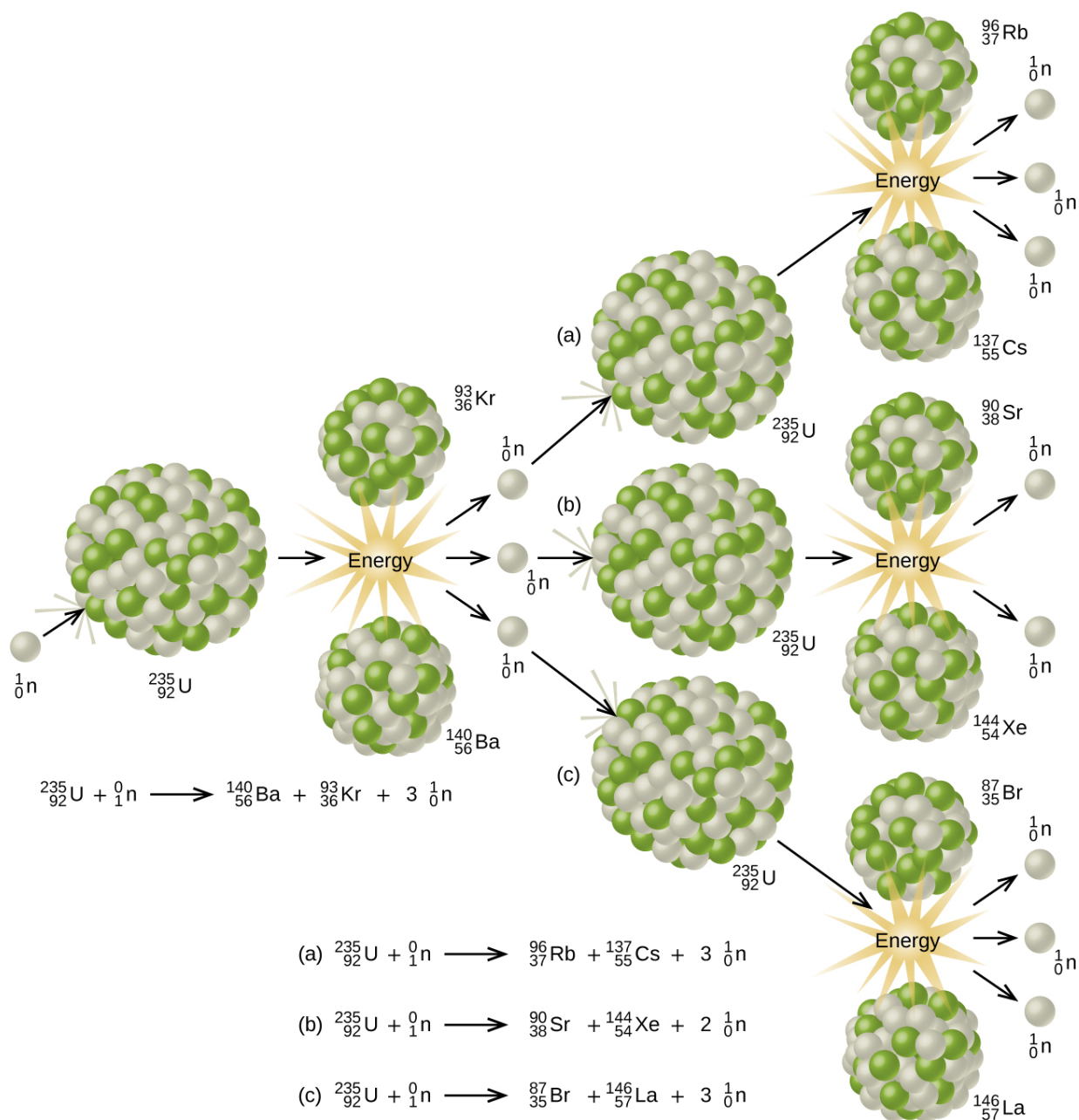
The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be **fissile** or **fissionable**. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission

becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a **critical mass**. An amount of fissionable material that cannot sustain a chain reaction is a **subcritical mass**. An amount of material in which there is an increasing rate of fission is known as a **supercritical mass**. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled ([link]).

Sub-critical mass   **Critical mass**

(a)   (b)
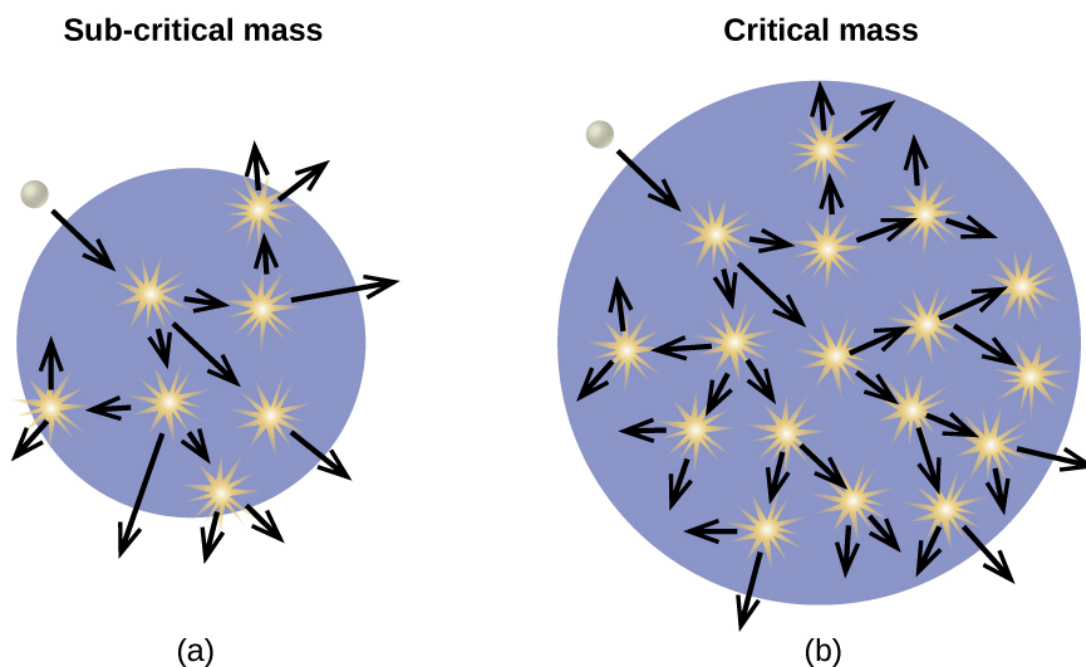
(a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb ([link]) contains several pounds of fissionable material, $^{235}_{92}\text{U}$ or $^{239}_{94}\text{Pu}$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together

quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.
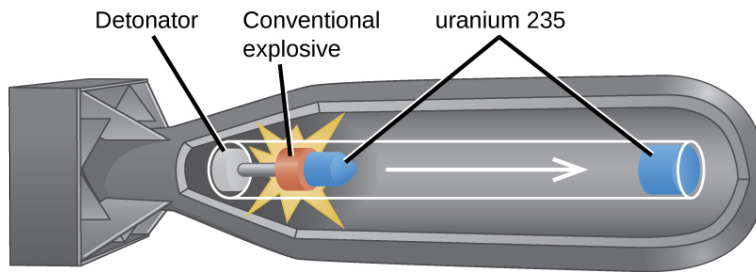
(a)
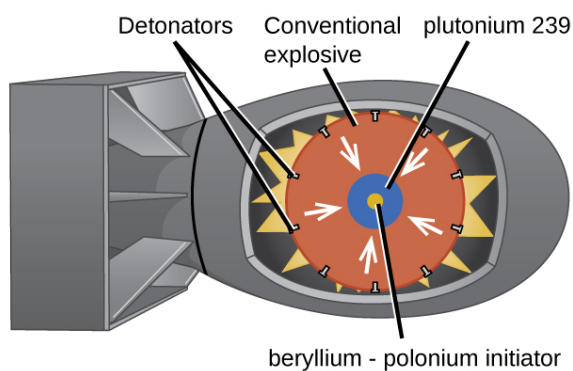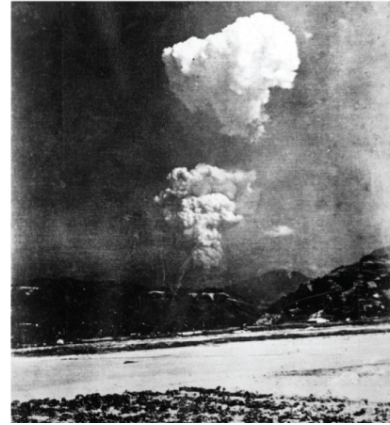
(b)

(a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a **nuclear reactor** ([link]). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.
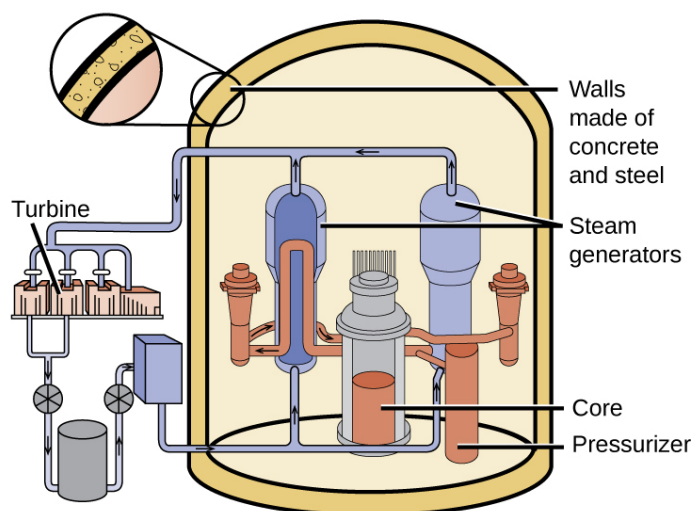
(a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by "Mike" Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham's law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (refer back to [link]). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A **nuclear moderator** is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water $\left(_1^2H_2O\right)$ or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear **reactor coolant** is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use

water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use **control rods** ([link]) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:
Equation:

$$\ce{^{10}_{5}B} + \ce{^{1}_{0}n} \longrightarrow \ce{^{7}_{3}Li} + \ce{^{4}_{2}He}$$
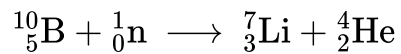
When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.
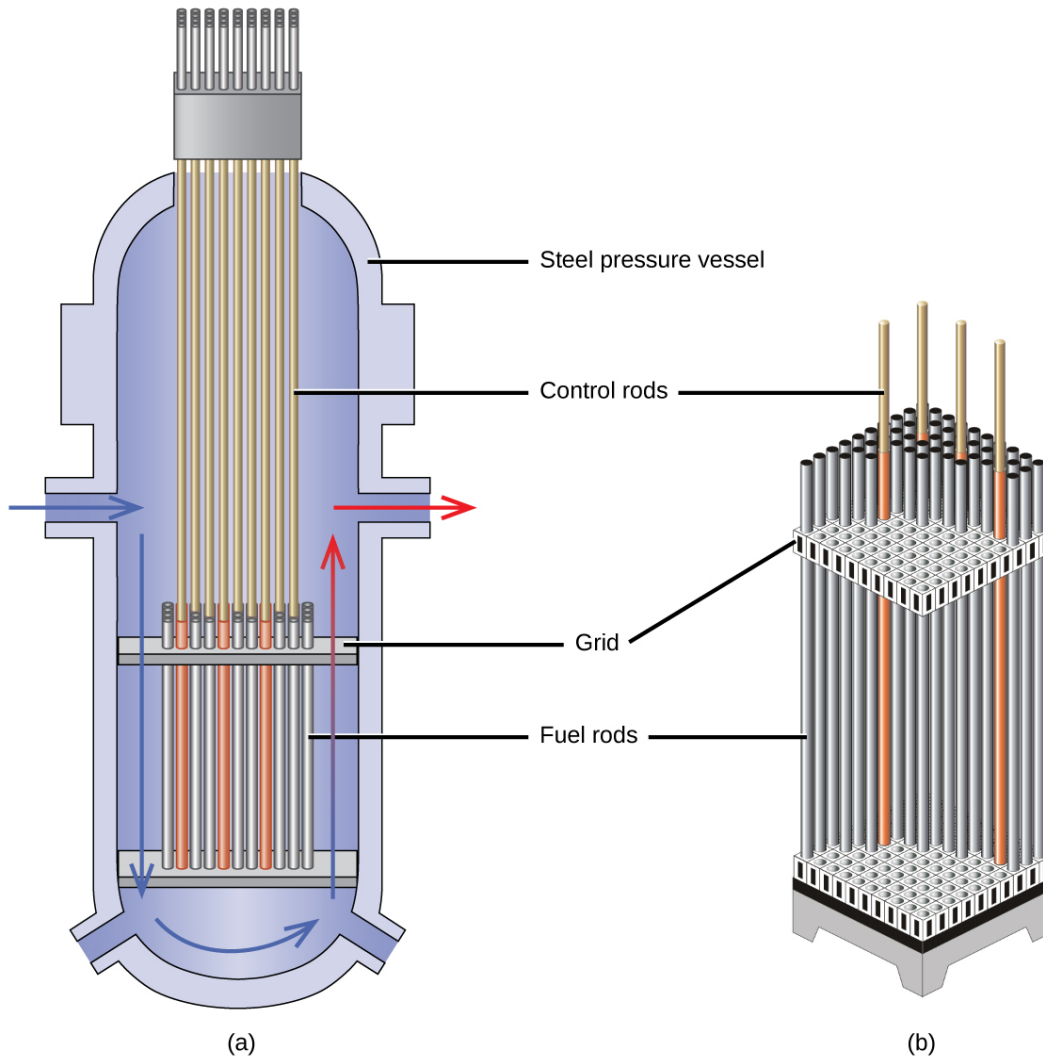
The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, http://glossary.periodni.com/glossary.php?en=control+rod)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a **containment system** (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Note:

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the

reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

Equation:

$$\mathrm{Zr}(s) + 2\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\mathrm{H_2}(g)$$
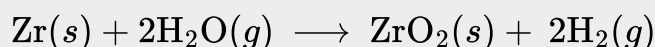
The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary ([link]).

(a)   (b)

(a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled ([link]).
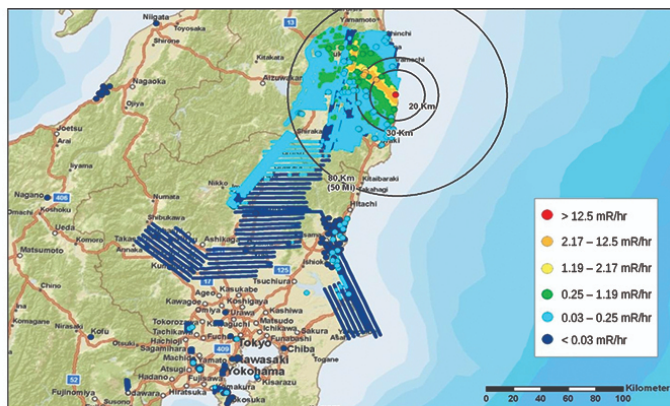
(a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Nuclear Fusion and Fusion Reactors

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called **fusion**. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

Equation:

$$4{}^{1}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\text{msubsup}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\text{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, msubsup and a triton, msubsup, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

Equation:

$${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2{}^{1}_{0}\text{n}$$
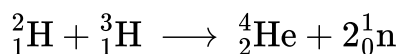
This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^{9} kilojoules per mole of ${}^{4}_{2}\text{He}$ formed. The very high temperature is

necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

Another much more beneficial way to create fusion reactions is in a **fusion reactor**, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams ([link]). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.
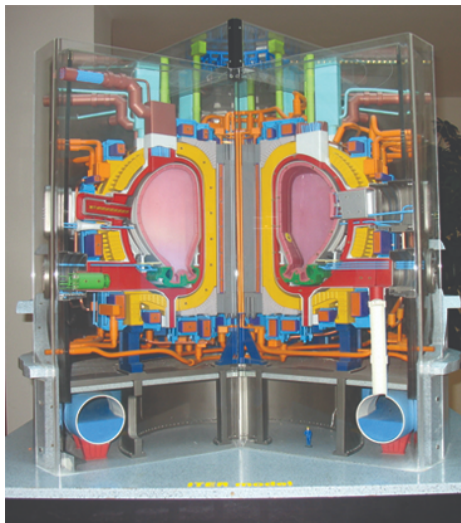
(a)
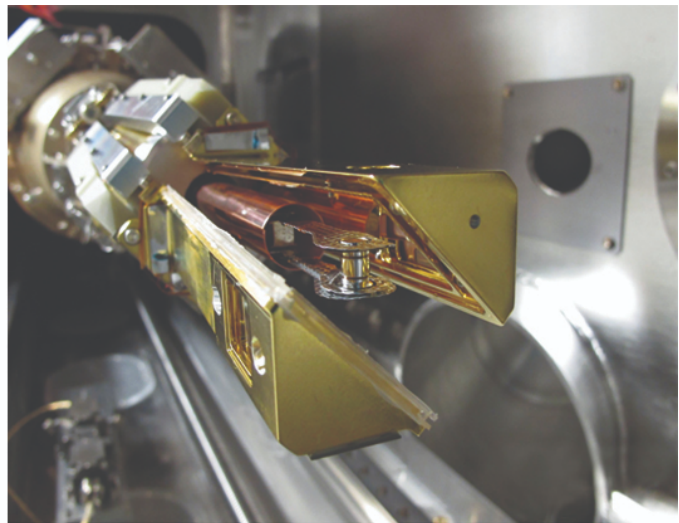
(b)

(a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Key Concepts and Summary

It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

Chemistry End of Chapter Exercises

Exercise:

  Problem:

  Write the balanced nuclear equation for the production of the following transuranium elements:

  (a) berkelium-244, made by the reaction of Am-241 and He-4

(b) fermium-254, made by the reaction of Pu-239 with a large number of neutrons

(c) lawrencium-257, made by the reaction of Cf-250 and B-11

(d) dubnium-260, made by the reaction of Cf-249 and N-15

Solution:

(a) $^{241}_{95}\text{Am} + {}^4_2\text{He} \longrightarrow {}^{244}_{97}\text{Bk} + {}^1_0\text{n}$; (b) $^{239}_{94}\text{Pu} + 15{}^1_0\text{n} \longrightarrow {}^{254}_{100}\text{Fm} + 6{}^0_{-1}\text{e}$;
(c) $^{250}_{98}\text{Cf} + {}^{11}_5\text{B} \longrightarrow {}^{257}_{103}\text{Lr} + 4$<mark style="background-color:yellow;color:red">msubsup</mark>; (d) $^{249}_{98}\text{Cf} + {}^{15}_7\text{N} \longrightarrow {}^{260}_{105}\text{Db} + 4{}^1_0\text{n}$
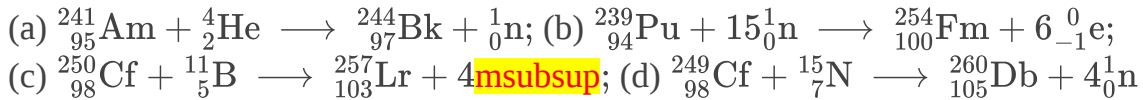
Exercise:

Problem:

How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

Exercise:

Problem:

Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

Solution:

Two nuclei must collide for fusion to occur. High temperatures are required to give the nuclei enough kinetic energy to overcome the very strong repulsion resulting from their positive charges.

Exercise:

Problem:

Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

Exercise:

Problem: Describe the components of a nuclear reactor.

Solution:

A nuclear reactor consists of the following:

1. A nuclear fuel. A fissionable isotope must be present in large enough quantities to sustain a controlled chain reaction. The radioactive isotope is contained in tubes called fuel rods.

2. A moderator. A moderator slows neutrons produced by nuclear reactions so that they can be absorbed by the fuel and cause additional nuclear reactions.

3. A coolant. The coolant carries heat from the fission reaction to an external boiler and turbine where it is transformed into electricity.

4. A control system. The control system consists of control rods placed between fuel rods to absorb neutrons and is used to adjust the number of neutrons and keep the rate of the chain reaction at a safe level.

5. A shield and containment system. The function of this component is to protect workers from radiation produced by the nuclear reactions and to withstand the high pressures resulting from high-temperature reactions.

Exercise:

Problem:

In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

Exercise:

Problem:

Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

Solution:

The fission of uranium generates heat, which is carried to an external steam generator (boiler). The resulting steam turns a turbine that powers an electrical generator.

Glossary

chain reaction
    repeated fission caused when the neutrons released in fission bombard other atoms

containment system

(also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

control rod
material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

critical mass
amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

fissile (or fissionable)
when a material is capable of sustaining a nuclear fission reaction

fission
splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

fusion
combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor
nuclear reactor in which fusion reactions of light nuclei are controlled

nuclear fuel
fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator
substance that slows neutrons to a speed low enough to cause fission

nuclear reactor
environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation
conversion of one nuclide into another nuclide

particle accelerator
device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

reactor coolant

    assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

subcritical mass

    amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

supercritical mass

    amount of material in which there is an increasing rate of fission

transmutation reaction

    bombardment of one type of nuclei with other nuclei or neutrons

transuranium element

    element with an atomic number greater than 92; these elements do not occur in nature

Uses of Radioisotopes
By the end of this section, you will be able to:

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a **radioactive tracer** (or **radioactive label**). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioisotopes have revolutionized medical practice (see Appendix M), where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 $\left(^{99}_{43}\text{Tc}\right)$, thallium-201 $\left(^{201}_{81}\text{Tl}\right)$, iodine-131 $\left(^{131}_{53}\text{I}\right)$, and sodium-24 $\left(^{24}_{11}\text{Na}\right)$. Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 ([link]) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.
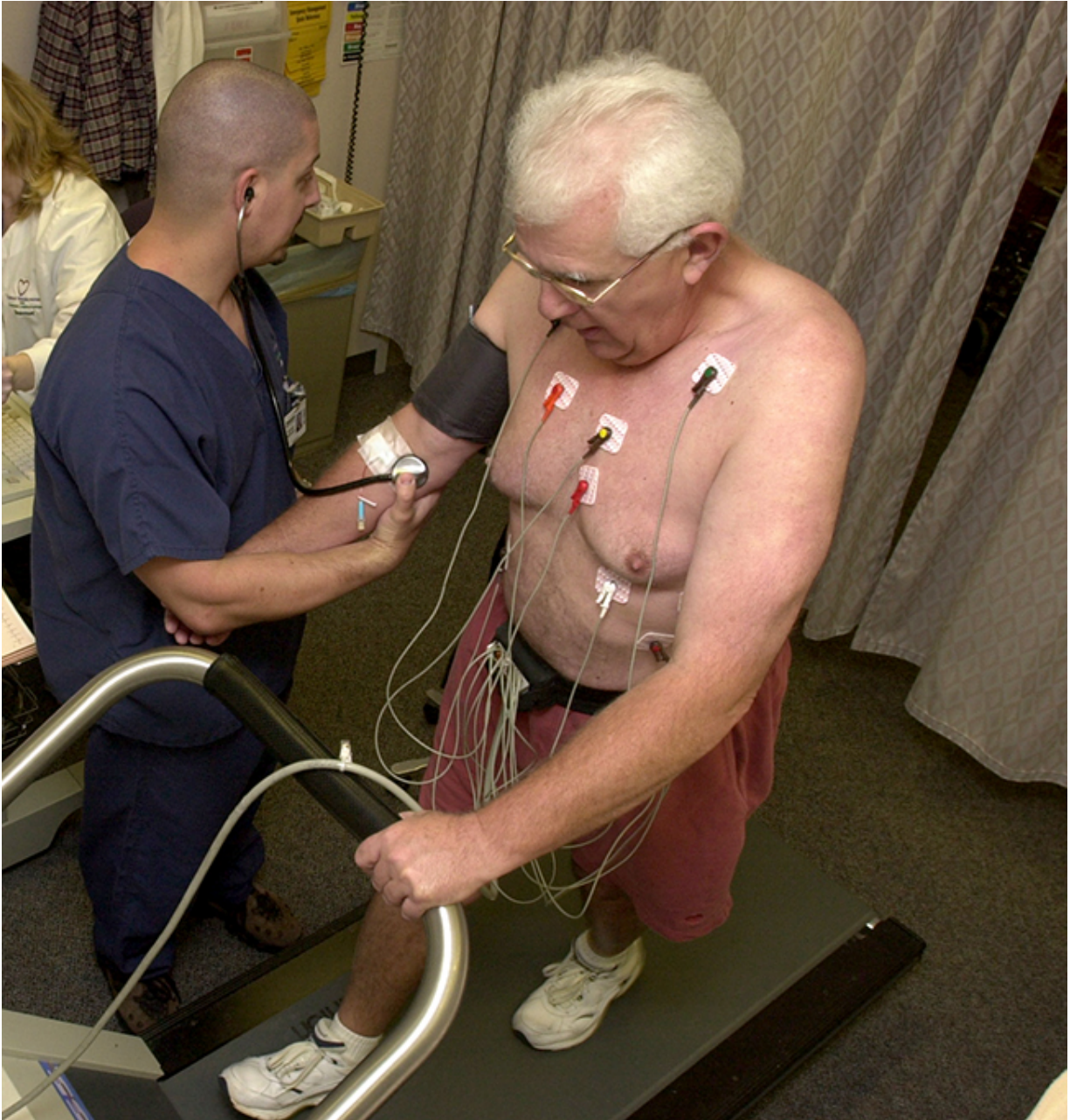
Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted ([link]). The parent nuclide Mo-99 is part of a molybdate ion, MoO_4^{2-}; when it decays, it forms the pertechnetate ion, TcO_4^-. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.
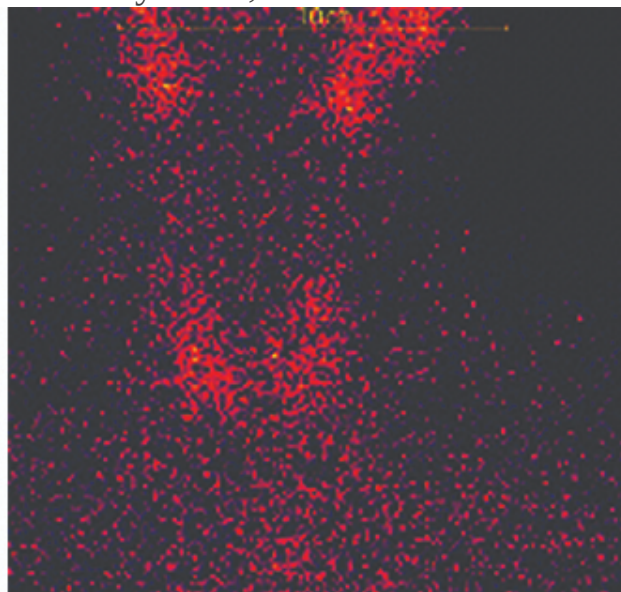
(a)   (b)

(a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The MoO_4^{2-} is retained by the matrix in the column, whereas the TcO_4^- passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. **Radiation therapy** is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing ([link]). A cancer patient may receive **external beam radiation therapy** delivered by a machine outside the body, or **internal radiation therapy (brachytherapy)** from a radioactive substance that has been introduced into the body. Note that **chemotherapy** is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.
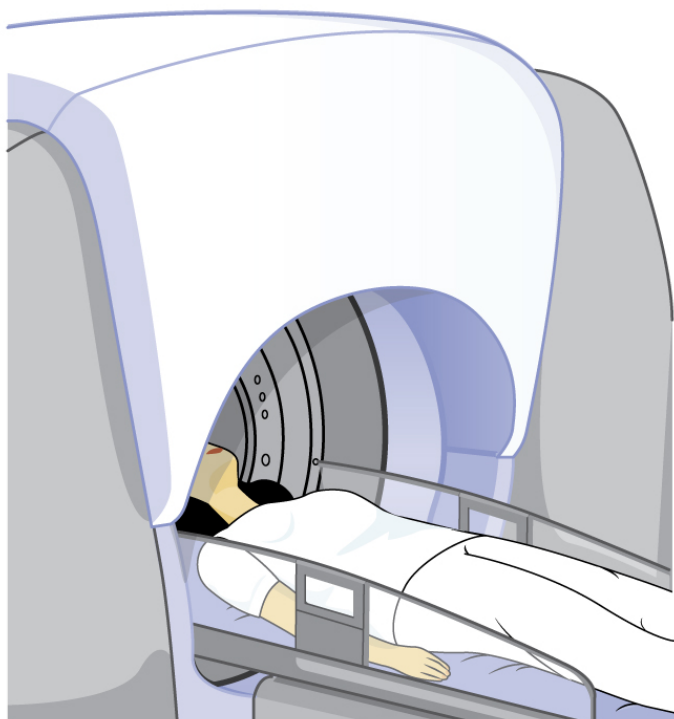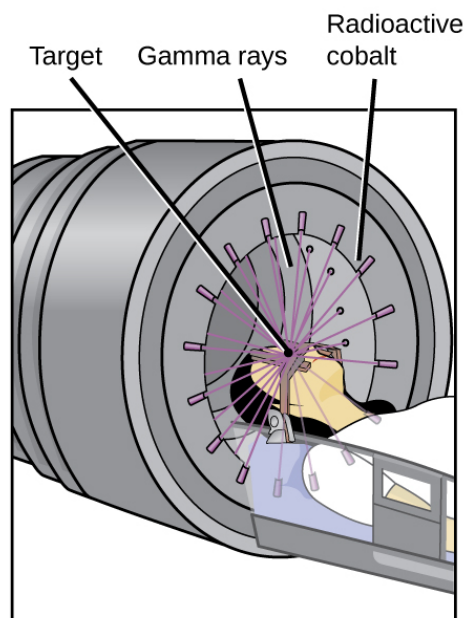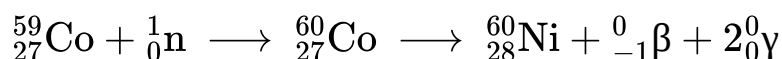

(a) (b)

The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

Equation:

$$\ce{^{59}_{27}Co + ^{1}_{0}n \longrightarrow ^{60}_{27}Co \longrightarrow ^{60}_{28}Ni + ^{0}_{-1}\beta + 2^{0}_{0}\gamma}$$

The overall decay scheme for this is shown graphically in [link].

$^{60}_{27}$Co — 5.272 a

0.31 MeV β
99.88%

1.48 MeV β
0.12%

1.1732 MeV γ

1.3325 MeV γ

$^{60}_{28}$Ni
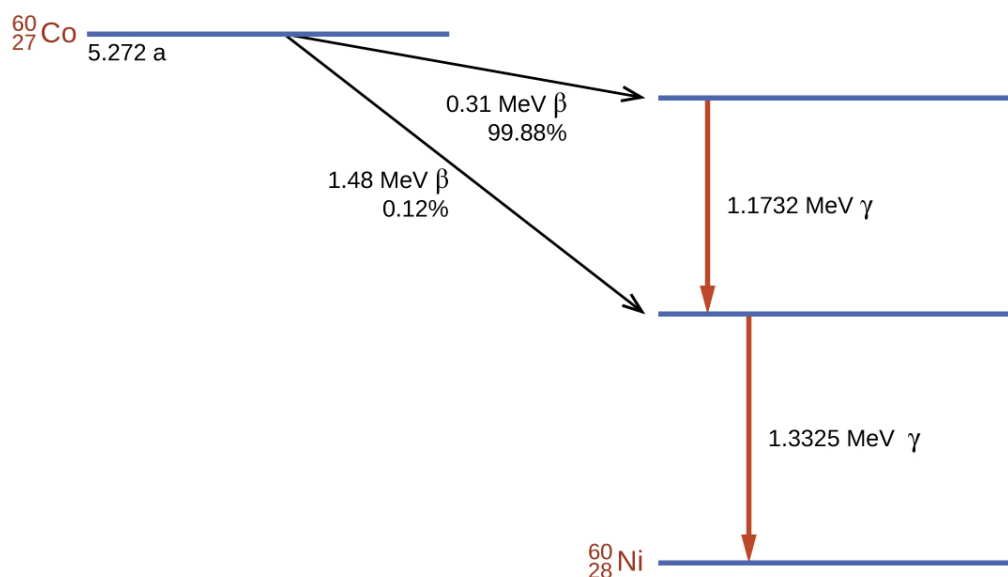
Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

Equation:

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g),$$
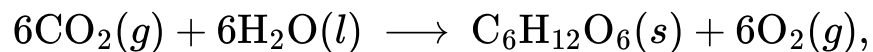
but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $^{14}_{6}C$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse ([link]). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

(a)   (b)

Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors ([link]). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.
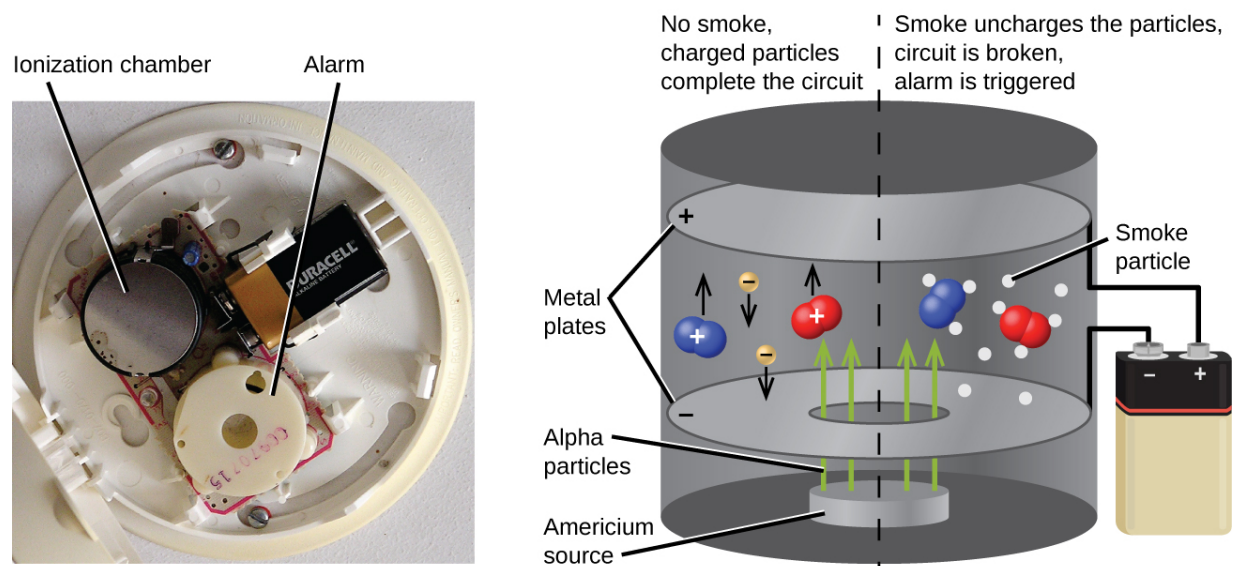
Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

Key Concepts and Summary

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other

applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-133 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β^- emission.

(a) Write an equation for the decay.

(b) How long will it take for a dose of I-131 to decay to 25.0% of its original amount?

Solution:

(a) $^{133}_{53}\text{I} \longrightarrow {}^{133}_{54}\text{Xe} + {}^{0}_{-1}\text{e}$; (b) 17.4 days

Glossary

chemotherapy
    similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

external beam radiation therapy
    radiation delivered by a machine outside the body

internal radiation therapy

(also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

radiation therapy

use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive tracer

(also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

Biological Effects of Radiation
By the end of this section, you will be able to:

- Describe the biological impact of ionizing radiation
- Define units for measuring radiation exposure
- Explain the operation of common tools for detecting radioactivity
- List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death ([link]).
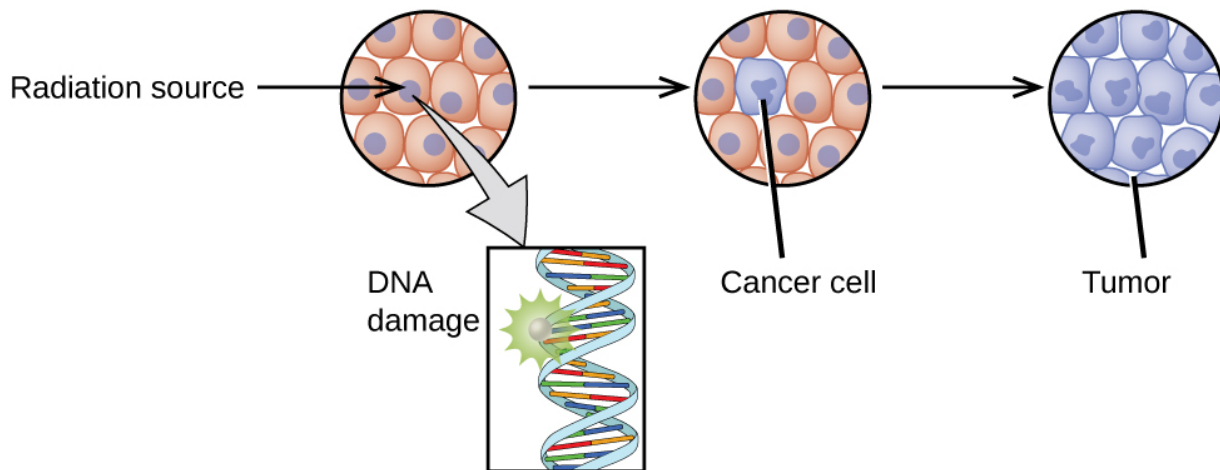
Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Ionizing and Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of **nonionizing radiation** (for example, light and microwaves) and **ionizing radiation**, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) ([link]).

Increasing energy E →				
Increasing frequency ν →				
← Increasing wavelength λ				

Non-ionizing			Ionizing	
Broadcast and wireless radio	Microwave	Terahertz	Infrared	Visible light	Ultraviolet	X-ray	Gamma

Non-thermal	**Thermal**	**Optical**	**Broken bonds**
Induces low currents	Induces high currents	Excites electrons	Damages DNA
	Heating	Photo-chemical effects	

| Static field | Power line | AM radio | FM radio | Microwave oven | Heat lamp | Tanning booth | Medical x-rays |

Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting

their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + radiation \xrightarrow{\quad e^- \quad} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$
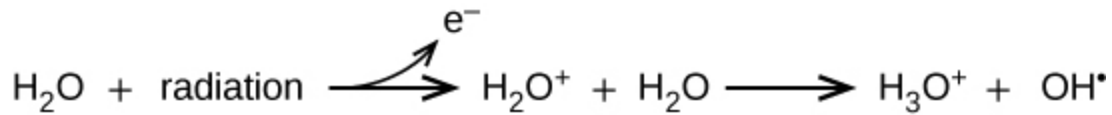
Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in [link].
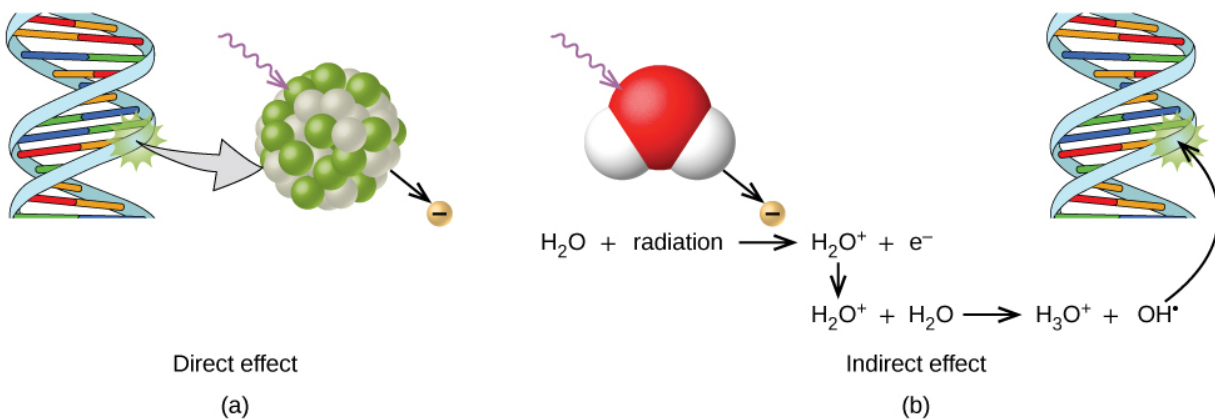

Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material ([link]). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.
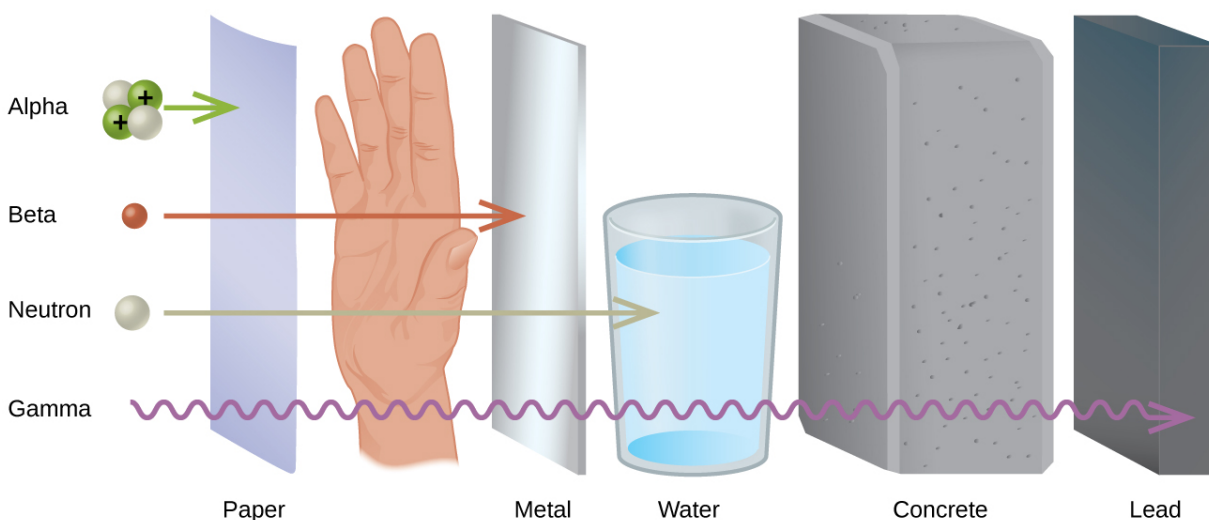
The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

Note:

Radon Exposure

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238 ([link]), which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings ([link]).
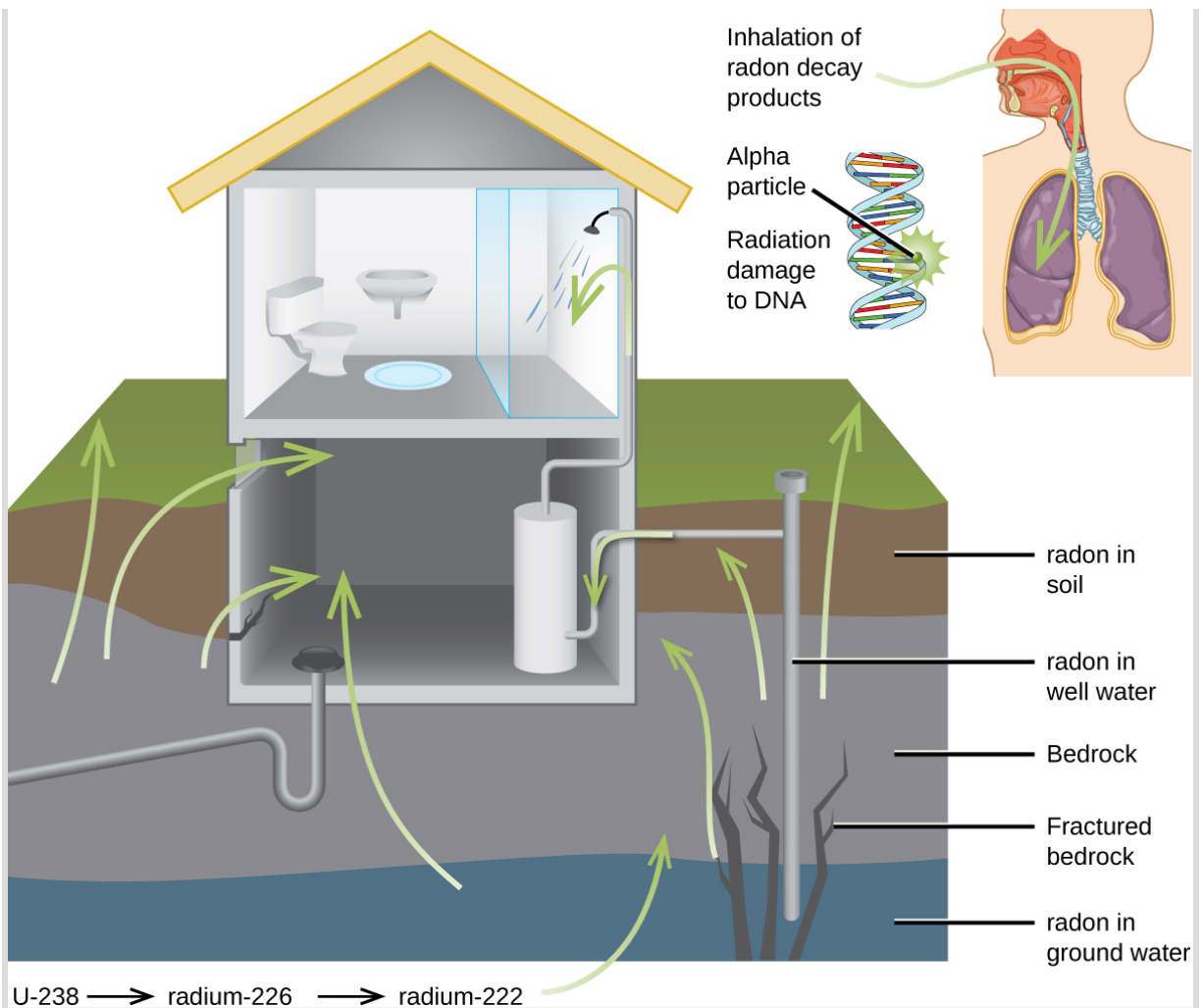
Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and

the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters ([link]). Probably the best-known radiation instrument, the **Geiger counter** (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A **scintillation counter** contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. **Radiation dosimeters** also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.
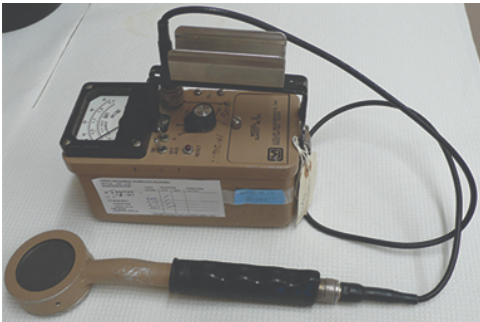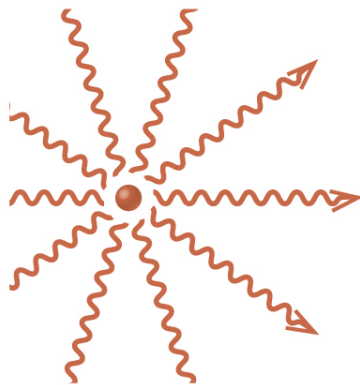

Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons)

A variety of units are used to measure various aspects of radiation ([link]). The SI unit for rate of radioactive decay is the **becquerel (Bq)**, with 1 Bq = 1 disintegration per second. The **curie (Ci)** and **millicurie (mCi)** are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the **gray (Gy)**, with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the **radiation absorbed dose (rad)** is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the **sievert (Sv)**. This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose. The **roentgen equivalent for man (rem)** is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the **RBE** (for **relative biological effectiveness**) that is an approximate measure of the relative damage done by the radiation. These are related by:

Equation:

$$\text{number of rems} = \text{RBE} \times \text{number of rads}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

Film badge or dosimeter measures tissue damage exposure in rems or sieverts

Rate of radioactive decay measured in bequerels or curies

Absorbed dose measured in grays or rads

Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.

Units of Radiation Measurement

[link] summarizes the units used for measuring radiation.

Units Used for Measuring Radiation			
Measurement Purpose	Unit	Quantity Measured	Description

Units Used for Measuring Radiation			
Measurement Purpose	**Unit**	**Quantity Measured**	**Description**
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE $\times$ Gy
	roentgen equivalent for man (rem)		Rem = RBE $\times$ rad

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in [link], the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical

exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

Radiation Doses and Regulatory Limits (in Millirems)
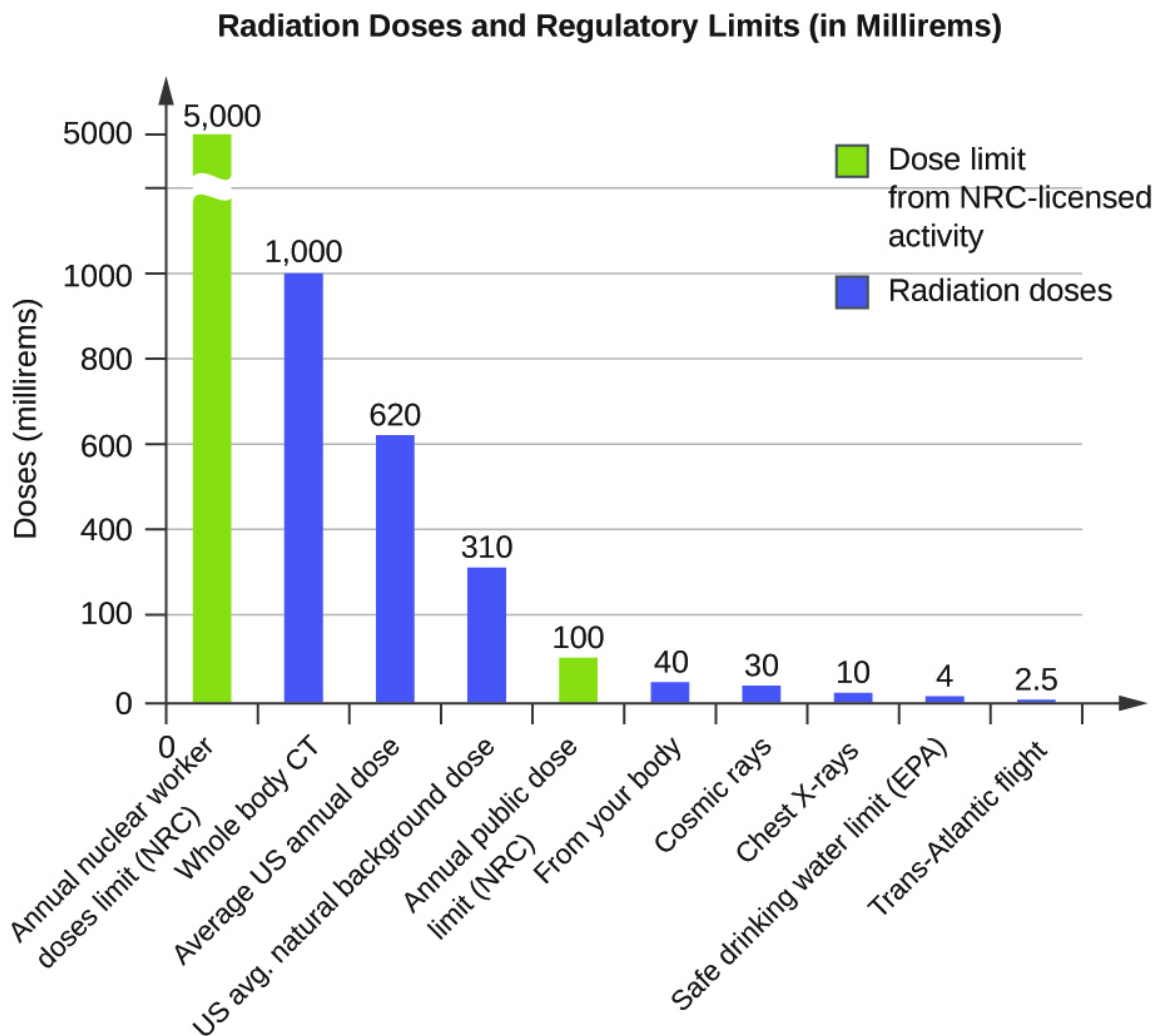
The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission)

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in [link].

Health Effects of Radiation[footnote] Source: US Environmental Protection Agency		
Exposure (rem)	**Health Effect**	**Time to Onset (without treatment)**
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—

Health Effects of Radiation[footnote] Source: US Environmental Protection Agency		
Exposure (rem)	**Health Effect**	**Time to Onset (without treatment)**
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Key Concepts and Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or

break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, and including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source, and limiting time of exposure.

Key Equations

- rem = RBE × rad
- Sv = RBE × Gy

Chemistry End of Chapter Exercises

Exercise:

Problem:

Based on what is known about Radon-222's primary decay method, why is inhalation so dangerous?

Solution:

Alpha particles can be stopped by very thin shielding but have much stronger ionizing potential than beta particles, X-rays, and γ-rays. When inhaled, there is no protective skin covering the cells of the

lungs, making it possible to damage the DNA in those cells and cause cancer.

Exercise:

Problem:

Given specimens uranium-232 ($t_{1/2}$ = 68.9 y) and uranium-233 ($t_{1/2}$ = 159,200 y) of equal mass, which one would have greater activity and why?

Glossary

becquerel (Bq)
　　SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

curie (Ci)
　　larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Geiger counter
　　instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

gray (Gy)
　　SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

ionizing radiation
　　radiation that can cause a molecule to lose an electron and form an ion

millicurie (mCi)
　　larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

nonionizing radiation
　　radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

radiation absorbed dose (rad)
    SI unit for measuring radiation dose, frequently used in medical
    applications; 1 rad = 0.01 Gy

radiation dosimeter
    device that measures ionizing radiation and is used to determine
    personal radiation exposure

relative biological effectiveness (RBE)
    measure of the relative damage done by radiation

roentgen equivalent man (rem)
    unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv

scintillation counter
    instrument that uses a scintillator—a material that emits light when
    excited by ionizing radiation—to detect and measure radiation

sievert (Sv)
    SI unit measuring tissue damage caused by radiation; takes into
    account energy and biological effects of radiation

Introduction
class="introduction"

- Electromagnetic Energy
- The Bohr Model
- Development of Quantum Theory
- Electronic Structure of Atoms (Electron Configurations)
- Periodic Variations in Element Properties

The Crab Nebula consists of remnants of a supernova (the explosion of a star). NASA's Hubble Space Telescope produced this composite image. Measurements of the emitted light wavelengths enabled astronomers to identify the elements in the nebula, determining that it contains specific ions including S^+

(green filaments) and O^{2+} (red filaments). (credit: modification of work by NASA and ESA)
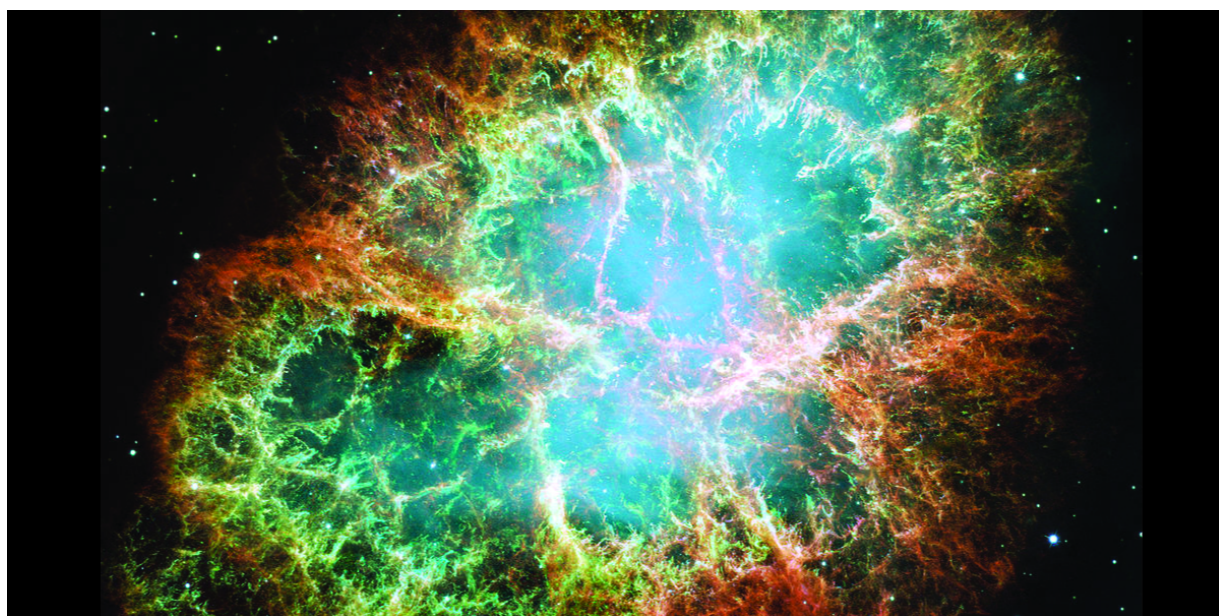
In 1054, Chinese astronomers recorded the appearance of a "guest star" in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula ([link]) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.

Electromagnetic Energy
By the end of this section, you will be able to:

- Explain the basic behavior of waves, including travelling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this

framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.
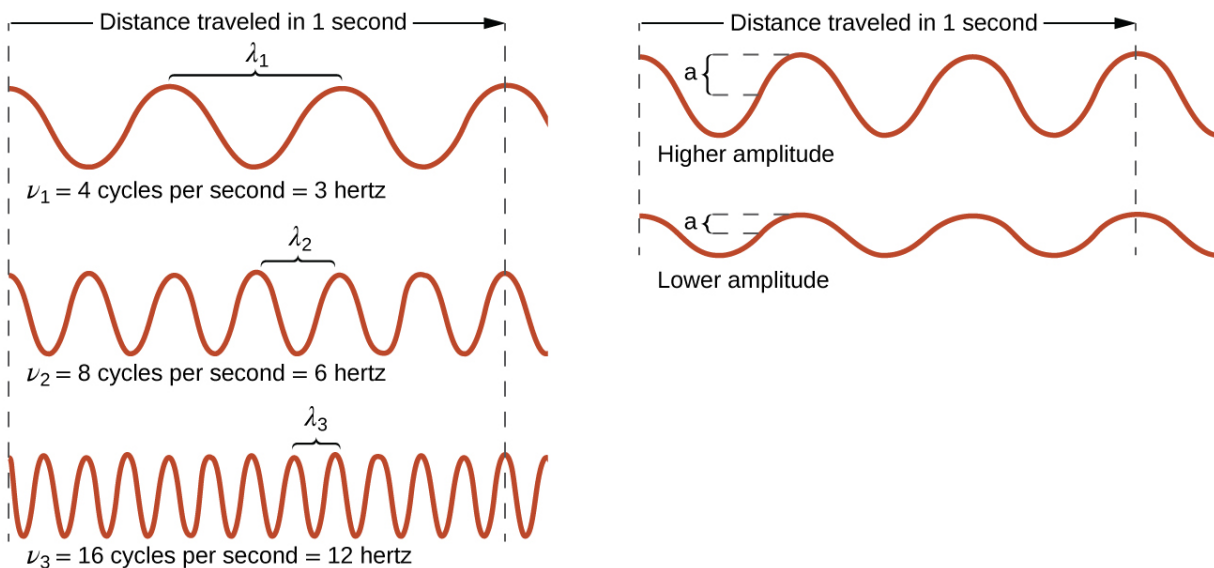
Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the

direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ, the lowercase Greek letter lambda), a **frequency** (denoted by v, the lowercase Greek letter nu), and an **amplitude**. As can be seen in [link], the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz (Hz)**. Common multiples of this unit are megahertz, (1 MHz = 1×10^6 Hz) and gigahertz (1 GHz = 1×10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in [link], this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

One-dimensional sinusoidal waves show the relationship among

wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (v), λv, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

Equation:

$$c = 2.998 \times 10^8 \text{ms}^{-1} = \lambda \nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in [link]. This figure also shows the **electromagnetic spectrum**, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).
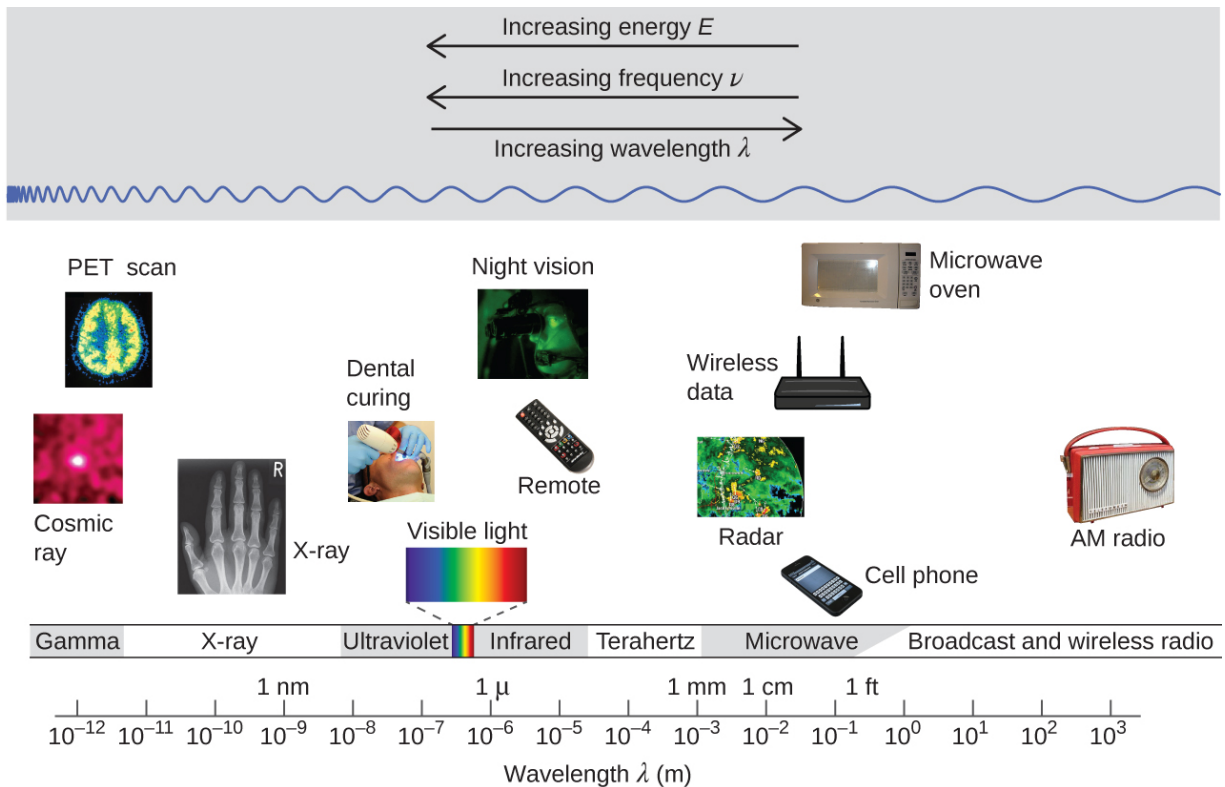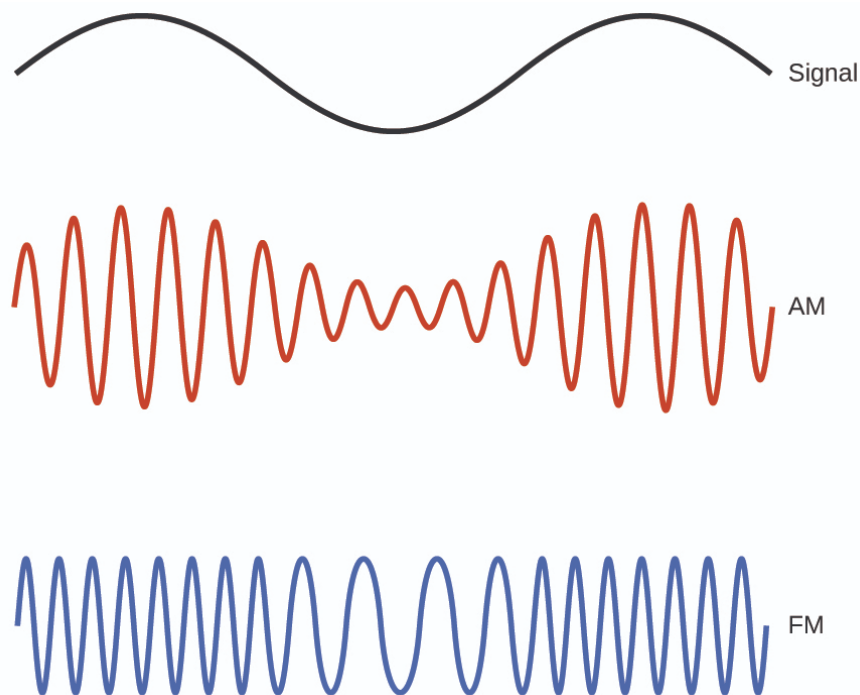
Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit "Cosmic ray": modification of work by NASA; credit "PET scan": modification of work by the National Institute of Health; credit "X-ray": modification of work by Dr. Jochen Lengerke; credit "Dental curing": modification of work by the Department of the Navy; credit "Night vision": modification of work by the Department of the Army; credit "Remote": modification of work by Emilian Robert Vicol; credit "Cell phone": modification of work by Brett Jordan; credit "Microwave oven": modification of work by Billy Mabray; credit "Ultrasound": modification of work by Jane Whitney; credit "AM radio": modification of work by Dave Clausen)

Note:

Wireless Communication

Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave ([link]). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

Note:

Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the

electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Line Spectra

A paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in [link], sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by

blackbody radiation curves at some appropriate temperature, such as those shown in [link].

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in [link]. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way ([link]). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.

Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in [link].
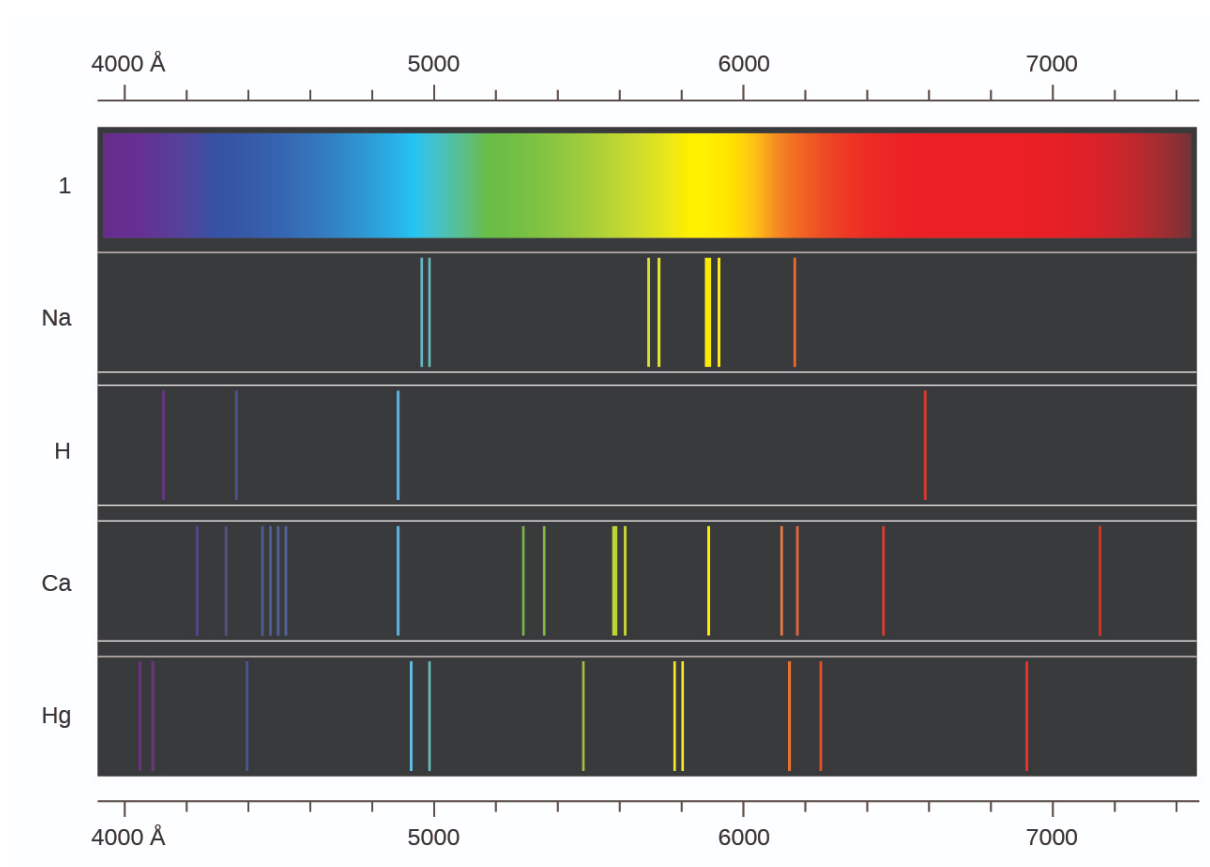
Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which k is a constant:

Equation:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right), \ n = 3, \ 4, \ 5, \ 6$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant (1.097×10^7 m^{-1}).

Equation:

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

Key Concepts and Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998×10^8 m s^{-1}. This radiation shows

wavelike behavior, which can be characterized by a frequency, ν, and a wavelength, λ, such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $E = \frac{hc}{\lambda}$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34}$ J s
- $\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

Chemistry End of Chapter Exercises

Exercise:

Problem:

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

Solution:

The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

Exercise:

Problem:

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

Solution:

Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

Exercise:

Problem: Answer the following question about a Blu-ray laser:

(a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?

Glossary

amplitude
>   extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

blackbody
>   idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

continuous spectrum
>   electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

electromagnetic radiation
>   energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum
>   range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

frequency (v)
>   number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)
>   the unit of frequency, which is the number of cycles per second, s^{-1}

intensity
>   property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern
    pattern typically consisting of alternating bright and dark fringes; it
    results from constructive and destructive interference of waves

line spectrum
    electromagnetic radiation emitted at discrete wavelengths by a specific
    atom (or atoms) in an excited state

node
    any point of a standing wave with zero amplitude

photon
    smallest possible packet of electromagnetic radiation, a particle of
    light

quantization
    occurring only in specific discrete values, not continuous

standing wave
    (also, stationary wave) localized wave phenomenon characterized by
    discrete wavelengths determined by the boundary conditions used to
    generate the waves; standing waves are inherently quantized

wave
    oscillation that can transport energy from one point to another in space

wavelength (λ)
    distance between two consecutive peaks or troughs in a wave

wave-particle duality
    term used to describe the fact that elementary particles including
    matter exhibit properties of both particles (including localized position,
    momentum) and waves (including nonlocalization, wavelength,
    frequency)

The Bohr Model
By the end of this section, you will be able to:

- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. The electrostatic force has the same form as the gravitational force between two mass particles except that the electrostatic force depends on the magnitudes of the charges on the particles (+1 for the proton and −1 for the electron) instead of the magnitudes of the particle masses that govern the gravitational force. Since forces can be derived from potentials, it is convenient to work with potentials instead, since they are forms of energy. The electrostatic potential is also called the Coulomb potential. Because the electrostatic potential has the same form as the gravitational potential, according to classical mechanics, the equations of motion should be similar, with the electron moving around the nucleus in circular or elliptical orbits (hence the label "planetary" model of the atom). This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the

classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

Equation:

$$| \Delta E | = | E_\mathrm{f} - E_\mathrm{i} | = h\nu = \frac{hc}{\lambda}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values for the angular momentum, energy, and orbit radius, Bohr assumed that only discrete values for these could occur (actually, quantizing any one of these would imply that the other two are also quantized). Bohr's expression for the quantized energies is:

Equation:

$$E_n = -\frac{k}{n^2} , \; n = 1,\, 2,\, 3,\, \ldots$$

In this expression, k is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

Equation:

$$\Delta E = k \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda}$$
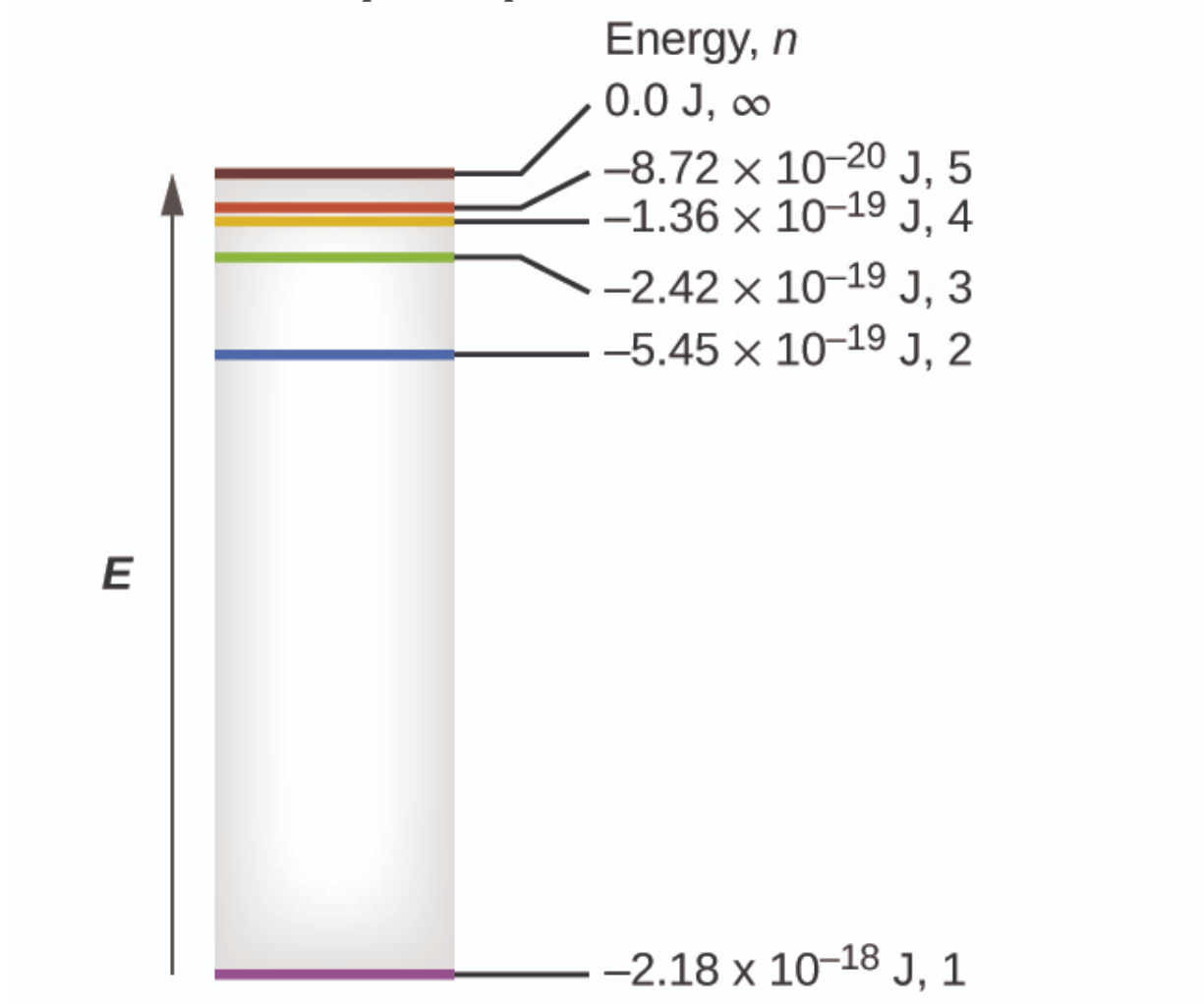
or

Equation:

$$\frac{1}{\lambda} = \frac{k}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

which is identical to the Rydberg equation for $R_\infty = \frac{k}{hc}$. When Bohr calculated his theoretical value for the Rydberg constant, R_∞, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that **Bohr's model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

The lowest few energy levels are shown in [link]. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its **ground electronic state** (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an **excited electronic state** (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state ([link]). In effect, an atom can "store" energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of energy, as the electron returns to its ground state (say, from $n = 5$ to $n = 1$), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from $n =$

5 to $n = 4$, emitting one quantum, then to $n = 1$, emitting a second quantum).

Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

Energy, n

0.0 J, ∞

-8.72×10^{-20} J, 5
-1.36×10^{-19} J, 4

-2.42×10^{-19} J, 3

-5.45×10^{-19} J, 2

E

-2.18×10^{-18} J, 1

Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

Energy, n

∞
5
4
3
2

E

1

Electron moves to higher energy as light is absorbed

Electron moves to lower energy as light is emitted
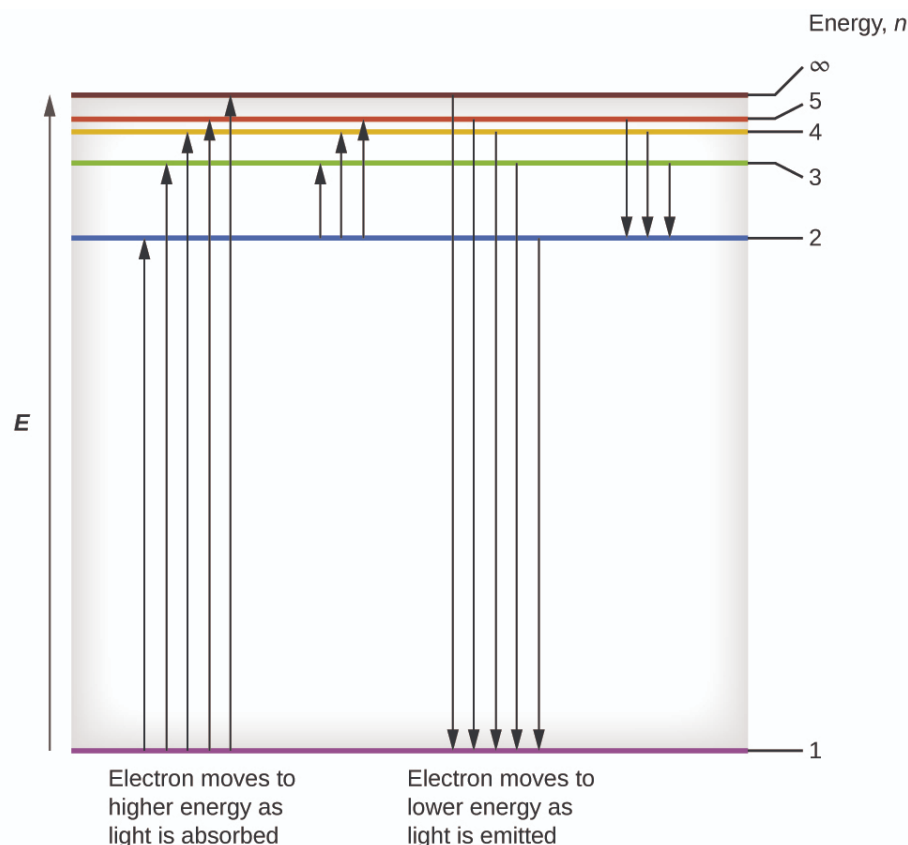
The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it is does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.

- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

Key Concepts and Summary

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

Exercise:

Problem:

What does it mean to say that the energy of the electrons in an atom is quantized?

Solution:

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

Exercise:

Problem:

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

Solution:

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature "solar system" with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The orbiting electron in Bohr's model is

assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

Exercise:

Problem:

The spectra of hydrogen and of calcium are shown in [link]. What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

Glossary

Bohr's model of the hydrogen atom
    structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

excited state
    state having an energy greater than the ground-state energy

ground state
    state in which the electrons in an atom, ion, or molecule have the lowest energy possible

quantum number
    integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

Molecular and Ionic Compounds
By the end of this section, you will be able to:

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions ([link]).
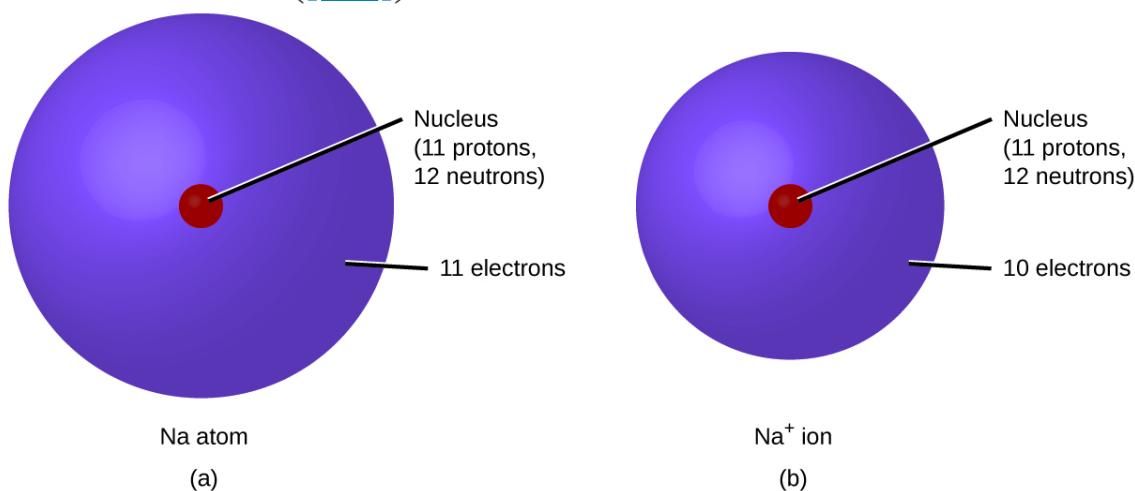
(a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas.

To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^-. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge ([link]). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

Periodic Table of the Elements

Period / **Group**

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		He
2	Li$^+$	Be^{2+}												C^{4-}	N^{3-}	O^{2-}	F$^-$	Ne
3	Na$^+$	Mg^{2+}											Al^{3+}		P^{3-}	S^{2-}	Cl$^-$	Ar
4	K$^+$	Ca^{2+}				Cr^{3+} Cr^{6+}	Mn^{2+}	Fe^{2+} Fe^{3+}	Co^{2+}	Ni^{2+}	Cu$^+$ Cu^{2+}	Zn^{2+}			As^{3-}	Se^{2-}	Br$^-$	Kr
5	Rb$^+$	Sr^{2+}									Ag$^+$	Cd^{2+}				Te^{2-}	I$^-$	Xe
6	Cs$^+$	Ba^{2+}								Pt^{2+}	Au$^+$ Au^{3+}	Hg$_2^{2+}$ Hg^{2+}					At$^-$	Rn
7	Fr$^+$	Ra^{2+}																

* ...

** ...

Some elements exhibit a regular pattern of ionic charge when they form ions.

Example:

Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

Check Your Learning

Give the symbol and name for the ion with 34 protons and 36 electrons.

Note:
Answer:
Se^{2-}, the selenide ion

Example:
Formation of Ions
Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution
Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

Check Your Learning
Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Note:
Answer:
Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in [link]. **Oxyanions** are polyatomic ions that contain one or more oxygen atoms.

Common Polyatomic Ions			
Name	**Formula**	**Related Acid**	**Formula**
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN

Common Polyatomic Ions

Name	Formula	Related Acid	Formula
azide	$N_3{}^-$	hydrazoic acid	HN_3
carbonate	$CO_3{}^{2-}$	carbonic acid	H_2CO_3
bicarbonate	$HCO_3{}^-$		
nitrate	$NO_3{}^-$	nitric acid	HNO_3
nitrite	$NO_2{}^-$	nitrous acid	HNO_2
sulfate	$SO_4{}^{2-}$	sulfiric acid	H_2SO_4
hydrogen sulfate	$HSO_4{}^-$		
sulfite	$SO_3{}^{2-}$	sulfurous acid	H_2SO_3
hydrogen sulfite	$HSO_3{}^-$		
phosphate	$PO_4{}^{3-}$	phosphoric acid	H_3PO_4
hydrogen phosphate	$HPO_4{}^{2-}$		
dihydrogen phosphate	$H_2PO_4{}^-$		
perchlorate	$ClO_4{}^-$	perchloric acid	$HClO_4$

Common Polyatomic Ions

Name	Formula	Related Acid	Formula
chlorate	ClO_3^-	chloric acid	$HClO_3$
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	$H_2Cr_2O_4$
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for "hyper") and *hypo-* (meaning "under") are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is ClO_4^-, chlorate is ClO_3^-, chlorite is ClO_2^- and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-}. This will be covered in more detail in the next module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the

bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct

electricity because its ions are able to move freely through the liquid ([link]).
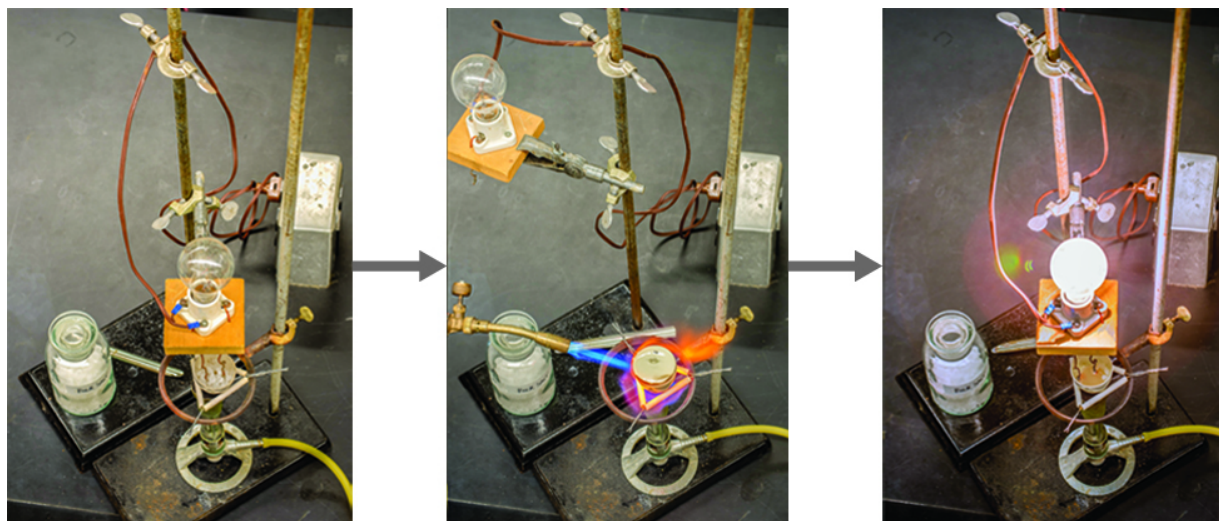
Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Note:

Watch this [video](#) to see a mixture of salts melt and conduct electricity.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example:
Predicting the Formula of an Ionic Compound
The gemstone sapphire ([link]) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?

Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

Check Your Learning

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Note:
Answer:

Na_2S

Many ionic compounds contain polyatomic ions ([link]) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $(PO_4{}^{3-})$ groups. The $PO_4{}^{3-}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example:
Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4{}^-$. What is the formula

of this compound?
Solution
The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.
Check Your Learning
Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, O_2^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Note:
Answer:
Li_2O_2
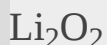
Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These **molecular compounds** (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example:
Predicting the Type of Bonding in Compounds
Predict whether the following compounds are ionic or molecular:
(a) KI, the compound used as a source of iodine in table salt
(b) H_2O_2, the bleach and disinfectant hydrogen peroxide
(c) $CHCl_3$, the anesthetic chloroform
(d) Li_2CO_3, a source of lithium in antidepressants
Solution
(a) Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
(b) Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.

(c) Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.
(d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

Check Your Learning

Using the periodic table, predict whether the following compounds are ionic or covalent:

(a) SO_2
(b) CaF_2
(c) N_2H_4
(d) $Al_2(SO_4)_3$

Note:
Answer:
(a) molecular; (b) ionic; (c) molecular; (d) ionic

Key Concepts and Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain

ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

Solution:

Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4

Exercise:

Problem:

Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.

Exercise:

Problem:

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

(a) NF_3

(b) BaO,

(c) $(NH_4)_2CO_3$

(d) $Sr(H_2PO_4)_2$

(e) IBr

(f) Na_2O

Solution:

(a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, NH_4^+, CO_3^{2-}; (d) ionic, Sr^{2+}, $H_2PO_4^-$; (e) covalent; (f) ionic, Na^+, O^{2-}

Exercise:

Problem:

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

(a) $KClO_4$

(b) $MgC_2H_3O_2$

(c) H_2S

(d) Ag_2S

(e) N_2Cl_4

(f) $Co(NO_3)_2$

Exercise:

Problem:

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

(a) Ca^{2+}, S^{2-}

(b) NH_4^+, SO_4^{2-}

(c) Al^{3+}, Br^-

(d) Na^+, HPO_4^{2-}
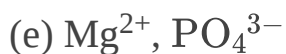
(e) Mg^{2+}, $PO_4{}^{3-}$

Solution:

(a) CaS; (b) $(NH_4)_2SO_4$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3 (PO_4)_2$

Exercise:

Problem:

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

(a) K^+, O^{2-}

(b) $NH_4{}^+$, $PO_4{}^{3-}$

(c) Al^{3+}, O^{2-}

(d) Na^+, $CO_3{}^{2-}$

(e) Ba^{2+}, $PO_4{}^{3-}$
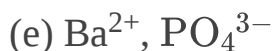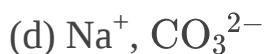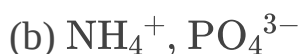
Glossary

covalent bond
> attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound
> (also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond
> electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound

compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound
(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion
ion composed of a single atom

oxyanion
polyatomic anion composed of a central atom bonded to oxygen atoms

polyatomic ion
ion composed of more than one atom

Chemical Nomenclature
By the end of this module, you will be able to:

- Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix –*ide*). Some examples are given in [link].

Names of Some Ionic Compounds	
NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an –*ide* ending, since the suffix is already present in the name of the anion. Examples are shown in [link].

Names of Some Polyatomic Ionic Compounds	
$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Everyday Ionic Compounds	
Ionic Compound	**Use**
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to "iodized" salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
$NaHCO_3$, sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na_2CO_3, sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
$CaCO_3$ calcium carbonate	ingredient in antacids

Everyday Ionic Compounds	
Ionic Compound	**Use**
$Mg(OH)_2$, magnesium hydroxide	ingredient in antacids
$Al(OH)_3$, aluminum hydroxide	ingredient in antacids
NaOH, sodium hydroxide	lye; used as drain cleaner
K_3PO_4, potassium phosphate	food additive (many purposes)
$MgSO_4$, magnesium sulfate	added to purified water
Na_2HPO_4, sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3, sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see [link]), and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, "iron chloride," will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral

in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in [link].

Names of Some Transition Metal Ionic Compounds	
Transition Metal Ionic Compound	**Name**
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes –*ic* and –*ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example:
Naming Ionic Compounds
Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

(a) Fe_2S_3
(b) CuSe
(c) GaN
(d) $CrCl_3$
(e) $Ti_2(SO_4)_3$

Solution
The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-}, N^{3-}, Cl^-, and SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{3+}, and Ti^{3+}. These charges are used in the names of the metal ions:
(a) iron(III) sulfide
(b) copper(II) selenide
(c) gallium(III) nitride
(d) chromium(III) chloride
(e) titanium(III) sulfate

Check Your Learning
Write the formulas of the following ionic compounds:
(a) chromium(III) phosphide
(b) mercury(II) sulfide
(c) manganese(II) phosphate
(d) copper(I) oxide
(e) chromium(VI) fluoride

Note:
Answer:
(a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) CrF_6

Note:
Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich ([link]) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.
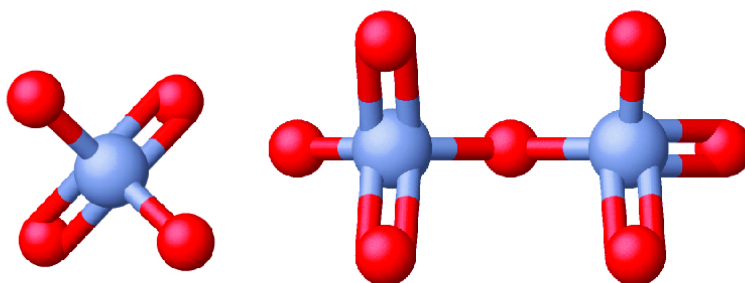
(a)   (b)

(a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, $CrO_4{}^{2-}$ (left), and dichromate, $Cr_2O_7{}^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. But Cr(VI) is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix –*ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in [link].

Nomenclature Prefixes

Number	Prefix		Number	Prefix
1 (sometimes omitted)	mono-		6	hexa-
2	di-		7	hepta-
3	tri-		8	octa-
4	tetra-		9	nona-
5	penta-		10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in [link].

Names of Some Molecular Compounds Composed of Two Elements

Compound	Name		Compound	Name
SO_2	sulfur dioxide		BCl_3	boron trichloride
SO_3	sulfur trioxide		SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide		PF_5	phosphorus pentafluoride

Names of Some Molecular Compounds Composed of Two Elements				
Compound	Name		Compound	Name
N_2O_4	dinitrogen tetroxide		P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide		IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.)

Example:
Naming Covalent Compounds
Name the following covalent compounds:
(a) SF_6
(b) N_2O_3
(c) Cl_2O_7
(d) P_4O_6
Solution
Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:
(a) sulfur hexafluoride
(b) dinitrogen trioxide
(c) dichlorine heptoxide
(d) tetraphosphorus hexoxide
Check Your Learning
Write the formulas for the following compounds:
(a) phosphorus pentachloride
(b) dinitrogen monoxide
(c) iodine heptafluoride

(d) carbon tetrachloride

Note:
Answer:
(a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

Note:

The following website provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as acids. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*

2. The other nonmetallic element name is modified by adding the suffix -*ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in [link].

Names of Some Simple Acids	
Name of Gas	**Name of Acid**
HF(g), hydrogen fluoride	HF(aq), hydrofluoric acid
HCl(g), hydrogen chloride	HCl(aq), hydrochloric acid
HBr(g), hydrogen bromide	HBr(aq), hydrobromic acid
HI(g), hydrogen iodide	HI(aq), hydroiodic acid
H_2S(g), hydrogen sulfide	H_2S(aq), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as **oxyacids**, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn

the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace –*ate* with –*ic*, or –*ite* with –*ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the –*ate* of carbonate is replace with –*ic*; and acid is added—so its name is carbonic acid. Other examples are given in [link]. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Names of Common Oxyacids		
Formula	**Anion Name**	**Acid Name**
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid

Names of Common Oxyacids		
Formula	**Anion Name**	**Acid Name**
H_3PO_4	phosphate	phosphoric acid

Key Concepts and Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion to *–ic*, and adding "acid;" H_2CO_3 is carbonic acid.

Chemistry End of Chapter Exercises

Exercise:

Problem: Name the following compounds:

(a) CsCl

(b) BaO

(c) K_2S

(d) $BeCl_2$

(e) HBr

(f) AlF_3

Solution:

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

Exercise:

Problem: Name the following compounds:

(a) NaF

(b) Rb_2O

(c) BCl_3

(d) H_2Se

(e) P_4O_6

(f) ICl_3

Exercise:

Problem: Write the formulas of the following compounds:

(a) rubidium bromide

(b) magnesium selenide

(c) sodium oxide

(d) calcium chloride

(e) hydrogen fluoride

(f) gallium phosphide

(g) aluminum bromide

(h) ammonium sulfate

Solution:

(a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$

Exercise:

Problem: Write the formulas of the following compounds:

(a) lithium carbonate

(b) sodium perchlorate

(c) barium hydroxide

(d) ammonium carbonate

(e) sulfuric acid

(f) calcium acetate

(g) magnesium phosphate

(h) sodium sulfite

Exercise:

Problem: Write the formulas of the following compounds:

(a) chlorine dioxide

(b) dinitrogen tetraoxide

(c) potassium phosphide

(d) silver(I) sulfide

(e) aluminum nitride

(f) silicon dioxide

Solution:

(a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) AlN; (f) SiO_2

Exercise:

Problem: Write the formulas of the following compounds:

(a) barium chloride

(b) magnesium nitride

(c) sulfur dioxide

(d) nitrogen trichloride

(e) dinitrogen trioxide

(f) tin(IV) chloride

Exercise:

Problem:

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) Cr_2O_3

(b) $FeCl_2$

(c) CrO_3

(d) $TiCl_4$

(e) CoO

(f) MoS_2

Solution:

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) oxide; (f) molybdenum(IV) sulfide

Exercise:

Problem:

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) $NiCO_3$

(b) MoO_3

(c) $Co(NO_3)_2$

(d) V_2O_5

(e) MnO_2

(f) Fe_2O_3

Exercise:

Problem:

The following ionic compounds are found in common household products. Write the formulas for each compound:

(a) potassium phosphate

(b) copper(II) sulfate

(c) calcium chloride

(d) titanium dioxide

(e) ammonium nitrate

(f) sodium bisulfate (the common name for sodium hydrogen sulfate)

Solution:

(a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

Exercise:

Problem:

The following ionic compounds are found in common household products. Name each of the compounds:

(a) $Ca(H_2PO_4)_2$

(b) $FeSO_4$

(c) $CaCO_3$

(d) MgO

(e) $NaNO_2$

(f) KI

Exercise:

Problem: What are the IUPAC names of the following compounds?

(a) manganese dioxide

(b) mercurous chloride (Hg_2Cl_2)

(c) ferric nitrate [$Fe(NO_3)_3$]

(d) titanium tetrachloride

(e) cupric bromide ($CuBr_2$)

Solution:

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

Glossary

binary acid
     compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound
     compound containing two different elements.

nomenclature
     system of rules for naming objects of interest

oxyacid
     compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Introduction
class="introduction"

The water in a swimming pool is a complex mixture of substances whose relative amounts must be carefully maintained to ensure the health and comfort of people using the pool. (credit: modification of work by Vic Brincat)

Swimming pools have long been a popular means of recreation, exercise, and physical therapy. Since it is impractical to refill large pools with fresh water on a frequent basis, pool water is regularly treated with chemicals to prevent the growth of harmful bacteria and algae. Proper pool maintenance requires regular additions of various chemical compounds in carefully measured amounts. For example, the relative amount of calcium ion, Ca^{2+}, in the water should be maintained within certain limits to prevent eye irritation and avoid damage to the pool bed and plumbing. To maintain proper calcium levels, calcium cations are added to the water in the form of an ionic compound that also contains anions; thus, it is necessary to know both the relative amount of Ca^{2+} in the compound and the volume of water in the pool in order to achieve the proper calcium level. Quantitative aspects of the composition of substances (such as the calcium-containing compound) and mixtures (such as the pool water) are the subject of this chapter.

Measurements
By the end of this section, you will be able to:

- Explain the process of measurement
- Identify the three basic parts of a quantity
- Describe the properties and units of length, mass, volume, density, temperature, and time
- Perform basic unit calculations and conversions in the metric and other unit systems

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. (Scientific notation is also known as exponential notation; a review of this topic can be found in Appendix B.) For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98×10^5 kg. The mass of the average mosquito is about 0.0000025 kilograms, which can be written as 2.5×10^{-6} kg.

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect that the volume of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be

effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in [link]. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the **International System of Units** or **SI Units** (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Base Units of the SI System		
Property Measured	**Name of Unit**	**Symbol of Unit**
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI

system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in [link].

Common Unit Prefixes			
Prefix	**Symbol**	**Factor**	**Example**
femto	f	10^{-15}	1 femtosecond (fs) = 1×10^{-15} s (0.000000000000001 s)
pico	p	10^{-12}	1 picometer (pm) = 1×10^{-12} m (0.000000000001 m)
nano	n	10^{-9}	4 nanograms (ng) = 4×10^{-9} g (0.000000004 g)
micro	μ	10^{-6}	1 microliter (μL) = 1×10^{-6} L (0.000001 L)
milli	m	10^{-3}	2 millimoles (mmol) = 2×10^{-3} mol (0.002 mol)
centi	c	10^{-2}	7 centimeters (cm) = 7×10^{-2} m (0.07 m)
deci	d	10^{-1}	1 deciliter (dL) = 1×10^{-1} L (0.1 L)

Common Unit Prefixes			
Prefix	**Symbol**	**Factor**	**Example**
kilo	k	10^3	1 kilometer (km) = 1 × 10^3 m (1000 m)
mega	M	10^6	3 megahertz (MHz) = 3 × 10^6 Hz (3,000,000 Hz)
giga	G	10^9	8 gigayears (Gyr) = 8 × 10^9 yr (8,000,000,000 Gyr)
tera	T	10^{12}	5 terawatts (TW) = 5 × 10^{12} W (5,000,000,000,000 W)

Note:

Need a refresher or more practice with scientific notation? Visit this site to go over the basics of scientific notation.

SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in

1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

Length

The standard unit of **length** in both the SI and original metric systems is the **meter (m)**. A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard ([link]); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers (1 km = 1000 m = 10^3 m), whereas shorter distances can be reported in centimeters (1 cm = 0.01 m = 10^{-2} m) or millimeters (1 mm = 0.001 m = 10^{-3} m).
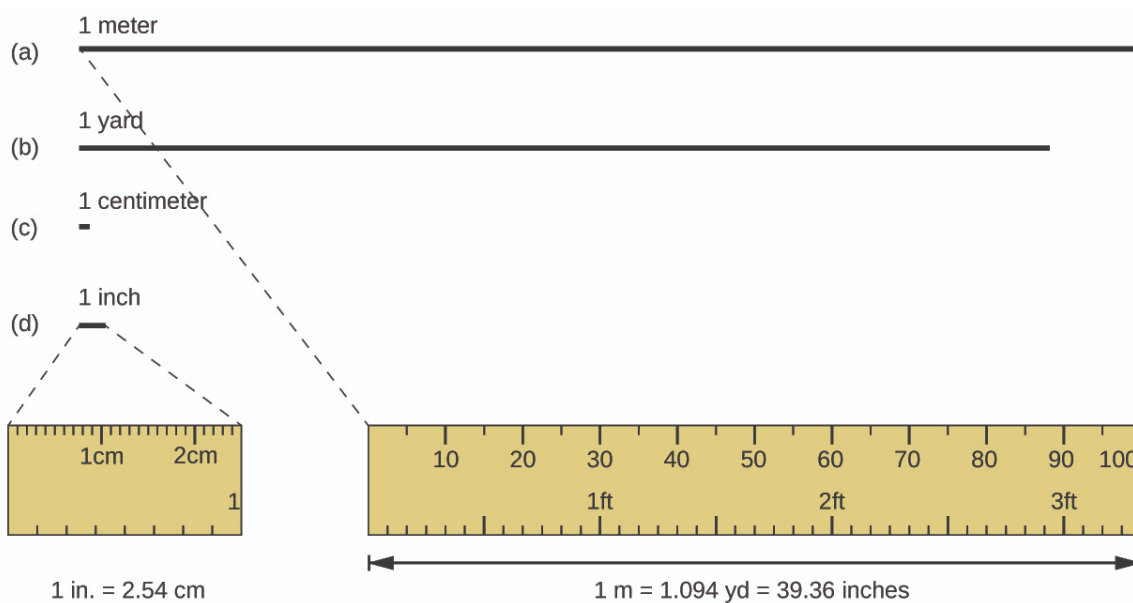
The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

The standard unit of mass in the SI system is the **kilogram (kg)**. A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France ([link]). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg).

This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National

Institutes of Standards and Technology)

Temperature

Temperature is an intensive property. The SI unit of temperature is the **kelvin (K)**. The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word "degree" nor the degree symbol (°). The degree **Celsius (°C)** is also allowed in the SI system, with both the word "degree" and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

Time

The SI base unit of time is the **second (s)**. Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 megaseconds = 5,000,000 s = 5×10^{6} s. Alternatively, hours, days, and years can be used.

Derived SI Units

We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length ([link]). The standard volume is a **cubic meter (m³)**, a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm³). A **liter (L)** is the more common name for the cubic decimeter. One liter is about 1.06 quarts.

A **cubic centimeter (cm³)** is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **c**ubic **c**entimeter) is often used by health professionals. A cubic centimeter is also called a **milliliter (mL)** and is 1/1000 of a liter.
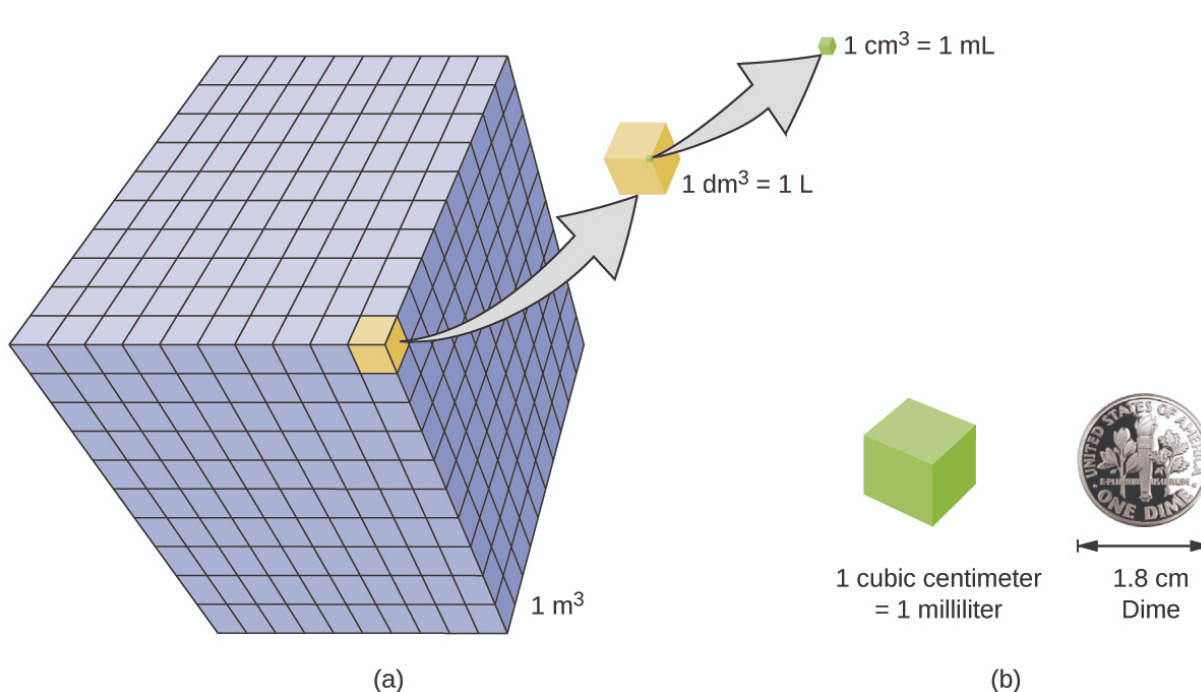
(a) The relative volumes are shown for cubes of 1 m³, 1 dm³ (1 L), and 1 cm³ (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm³ (1-mL) cube.

Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The **density** of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. [link] shows the densities of some common substances.

Densities of Common Substances		
Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L

Densities of Common Substances		
Solids	**Liquids**	**Gases (at 25 °C and 1 atm)**
copper 9.0 g/cm³	glycerin 1.26 g/cm³	carbon dioxide 1.80 g/L
lead 11.3 g/cm³	olive oil 0.92 g/cm³	helium 0.16 g/L
silver 10.5 g/cm³	gasoline 0.70–0.77 g/cm³	neon 0.83 g/L
gold 19.3 g/cm³	mercury 13.6 g/cm³	radon 9.1 g/L

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

Example:
Calculation of Density
Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its

density is not as great as that of gold, 19.3 g/cm^3. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

Equation:

$$\text{volume of lead cube} = 2.00 \text{ cm} \times 2.00 \text{ cm} \times 2.00 \text{ cm} = 8.00 \text{ cm}^3$$

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7 \text{ g}}{8.00 \text{ cm}^3} = \frac{11.3 \text{ g}}{1.00 \text{ cm}^3} = 11.3 \text{ g/cm}^3$$

(We will discuss the reason for rounding to the first decimal place in the next section.)

Check Your Learning

(a) To three decimal places, what is the volume of a cube (cm^3) with an edge length of 0.843 cm?

(b) If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?

Note:

Answer:

(a) 0.599 cm^3; (b) 8.91 g/cm^3

Note:

To learn more about the relationship between mass, volume, and density, use this interactive simulator to explore the density of different materials, like wood, ice, brick, and aluminum.

Example:
Using Displacement of Water to Determine Density
This PhET simulation illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.
Solution
When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.
The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:
Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{1.25 \text{ L}} = 4.00 \text{ kg/L}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:
Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00 \text{ kg}}{10.00 \text{ L}} = 0.500 \text{ kg/L}$$

Check Your Learning
Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank. Determine the density of the green block.

Note:
Answer:
2.00 kg/L

Key Concepts and Summary

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and g/cm^3 (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10^{-6} seconds) and megahertz (10^6 hertz), respectively.

Key Equations

- $\text{density} = \frac{\text{mass}}{\text{volume}}$

Chemistry End of Chapter Exercises

Exercise:

Problem: Is one liter about an ounce, a pint, a quart, or a gallon?

Exercise:

Problem: Is a meter about an inch, a foot, a yard, or a mile?

Solution:

about a yard

Exercise:

Problem:

Indicate the SI base units or derived units that are appropriate for the following measurements:

(a) the length of a marathon race (26 miles 385 yards)

(b) the mass of an automobile

(c) the volume of a swimming pool

(d) the speed of an airplane

(e) the density of gold

(f) the area of a football field

(g) the maximum temperature at the South Pole on April 1, 1913

Exercise:

Problem:

Indicate the SI base units or derived units that are appropriate for the following measurements:

(a) the mass of the moon

(b) the distance from Dallas to Oklahoma City

(c) the speed of sound

(d) the density of air

(e) the temperature at which alcohol boils

(f) the area of the state of Delaware

(g) the volume of a flu shot or a measles vaccination

Solution:

(a) kilograms; (b) meters; (c) kilometers/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

Exercise:

Problem:

Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.

(a) 10^3

(b) 10^{-2}

(c) 0.1

(d) 10^{-3}

(e) 1,000,000

(f) 0.000001

Exercise:

Problem:

Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

(a) c

(b) d

(c) G

(d) k

(e) m

(f) n

(g) p

(h) T

Solution:

(a) centi-, $\times\ 10^{-2}$; (b) deci-, $\times\ 10^{-1}$; (c) Giga-, $\times\ 10^{9}$; (d) kilo-, $\times\ 10^{3}$; (e) milli-, $\times\ 10^{-3}$; (f) nano-, $\times\ 10^{-9}$; (g) pico-, $\times\ 10^{-12}$; (h) tera-, $\times\ 10^{12}$

Exercise:

Problem:

A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

(a) Determine the density of this piece of jewelry.

(b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

Exercise:

Problem:

Visit this [PhET density simulation](#) and select the Same Volume Blocks.

(a) What are the mass, volume, and density of the yellow block?

(b) What are the mass, volume and density of the red block?

(c) List the block colors in order from smallest to largest mass.

(d) List the block colors in order from lowest to highest density.

(e) How are mass and density related for blocks of the same volume?

Solution:

(a) 8.00 kg, 5.00 L, 1.60 kg/L; (b) 2.00 kg, 5.00 L, 0.400 kg/L; (c) red < green < blue < yellow; (d) If the volumes are the same, then the density is directly proportional to the mass.

Exercise:

Problem:

Visit this [PhET density simulation](#) and select Custom Blocks and then My Block.

(a) Enter mass and volume values for the block such that the mass in kg is *less than* the volume in L. What does the block do? Why? Is this always the case when mass < volume?

(b) Enter mass and volume values for the block such that the mass in kg is *more than* the volume in L. What does the block do? Why? Is this always the case when mass > volume?

(c) How would (a) and (b) be different if the liquid in the tank were ethanol instead of water?

(d) How would (a) and (b) be different if the liquid in the tank were mercury instead of water?

Exercise:

Problem:

Visit this [PhET density simulation](#) and select Mystery Blocks.

(a) Pick one of the Mystery Blocks and determine its mass, volume, density, and its likely identity.

(b) Pick a different Mystery Block and determine its mass, volume, density, and its likely identity.

(c) Order the Mystery Blocks from least dense to most dense. Explain.

Solution:

(a) (b) Answer is one of the following. A/yellow: mass = 65.14 kg, volume = 3.38 L, density = 19.3 kg/L, likely identity = gold. B/blue: mass = 0.64 kg, volume = 1.00 L, density = 0.64 kg/L, likely identity = apple. C/green: mass = 4.08 kg, volume = 5.83 L, density = 0.700 kg/L, likely identity = gasoline. D/red: mass = 3.10 kg, volume = 3.38 L, density = 0.920 kg/L, likely identity = ice; and E/purple: mass = 3.53 kg, volume = 1.00 L, density = 3.53 kg/L, likely identity = diamond. (c) B/blue/apple (0.64 kg/L) < C/green/gasoline (0.700 kg/L) < C/green/ice (0.920 kg/L) < D/red/diamond (3.53 kg/L) < A/yellow/gold (19.3 kg/L)

Glossary

Celsius (°C)
>   unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm^3 or cc)
>   volume of a cube with an edge length of exactly 1 cm

cubic meter (m^3)
     SI unit of volume

density
     ratio of mass to volume for a substance or object

kelvin (K)
     SI unit of temperature; 273.15 K = 0 ºC

kilogram (kg)
     standard SI unit of mass; 1 kg = approximately 2.2 pounds

length
     measure of one dimension of an object

liter (L)
     (also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

meter (m)
     standard metric and SI unit of length; 1 m = approximately 1.094 yards

milliliter (mL)
     1/1,000 of a liter; equal to 1 cm^3

second (s)
     SI unit of time

SI units (International System of Units)
     standards fixed by international agreement in the International System
     of Units (*Le Système International d'Unités*)

unit
     standard of comparison for measurements

volume
     amount of space occupied by an object

Measurement Uncertainty, Accuracy, and Precision
By the end of this section, you will be able to:

- Define accuracy and precision
- Distinguish exact and uncertain numbers
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an **exact number**. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.
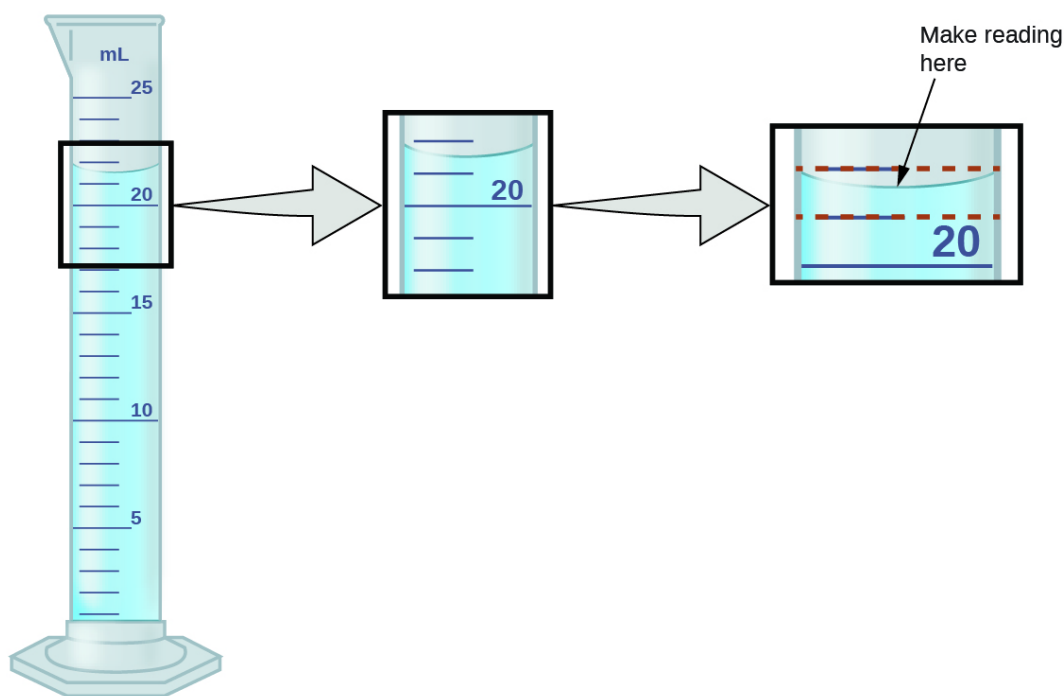
To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in [link]. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If we weigh the quarter on a more sensitive balance, we may find that its mass is 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some **uncertainty**, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called **significant figures** or **significant digits**. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them.
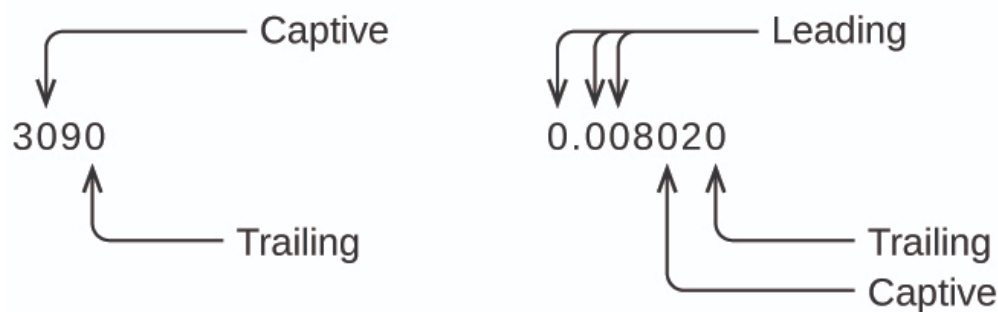
Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.

First nonzero figure on the left

1267 m

Four significant figures

First nonzero figure on the left

55.0 g

Three significant figures: note that the zero is to the right of the decimal point and therefore a significant figure

Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.

First nonzero figure on the left

70.607 mL

Five significant figures: all figures are measured including the two zeros

First nonzero figure on the left

0.00832407 mL

Six significant figures

The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.

Significant figures: clearly result of measurement

1300 g

These zeros could be significant (measured), or they could be placeholders

When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely when evaluating whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as 3.17×10^8 people.

Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for **rounding** numbers:

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we "round down" and leave the retained digit unchanged; if it is more than 5, we "round up" and increase the retained digit by 1; if the dropped digit *is* 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it's based on reliable statistics and is aimed at avoiding any bias when dropping the digit "5," since it is equally close to both possible values of the retained digit.)

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds "up" to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds "down" to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds "up" to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds "down" to 92.8 (the dropped digit is 5, and the retained digit is even)

Let's work through these rules with a few examples.

Example:
Rounding Numbers
Round the following to the indicated number of significant figures:
(a) 31.57 (to two significant figures)
(b) 8.1649 (to three significant figures)
(c) 0.051065 (to four significant figures)
(d) 0.90275 (to four significant figures)
Solution
(a) 31.57 rounds "up" to 32 (the dropped digit is 5, and the retained digit is even)
(b) 8.1649 rounds "down" to 8.16 (the dropped digit, 4, is less than 5)
(c) 0.051065 rounds "down" to 0.05106 (the dropped digit is 5, and the retained digit is even)
(d) 0.90275 rounds "up" to 0.9028 (the dropped digit is 5, and the retained digit is even)
Check Your Learning
Round the following to the indicated number of significant figures:
(a) 0.424 (to two significant figures)
(b) 0.0038661 (to three significant figures)
(c) 421.25 (to four significant figures)
(d) 28,683.5 (to five significant figures)

Example:
Addition and Subtraction with Significant Figures
Rule: When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (i.e., the least precise value in terms of addition and subtraction).
(a) Add 1.0023 g and 4.383 g.
(b) Subtract 421.23 g from 486 g.
Solution

(a)
$$\begin{array}{r} 1.0023 \text{ g} \\ + \ 4.383 \text{ g} \\ \hline 5.3853 \text{ g} \end{array}$$
Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)
$$\begin{array}{r} 486 \text{ g} \\ - \ 421.23 \text{ g} \\ \hline 64.77 \text{ g} \end{array}$$
Answer is 65 g (round to the ones place; no decimal places)

Check Your Learning
(a) Add 2.334 mL and 0.31 mL.
(b) Subtract 55.8752 m from 56.533 m.

In the midst of all these technicalities, it is important to keep in mind the reason why we use significant figures and rounding rules—to correctly represent the certainty of the values we report and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

$$\begin{aligned} V \ &= \ l \times w \times d \\ &= \ 13.44 \text{ dm} \ \times \ 5.920 \text{ dm} \ \times \ 2.54 \text{ dm} \\ &= \ 202.09459... \text{ dm}^3 \text{ (value from calculator)} \\ &= \ 202 \text{ dm}^3, \text{ or } 202 \text{ L} \ \text{(answer rounded to three significant figures)} \end{aligned}$$

Check Your Learning

What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Note:
Answer:
1.034 g/mL

Example:
Experimental Determination of Density Using Water Displacement

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.

Rebar mass = 69.658 g

"Final" volume = 22.4 mL

"Initial" volume = 13.5 mL
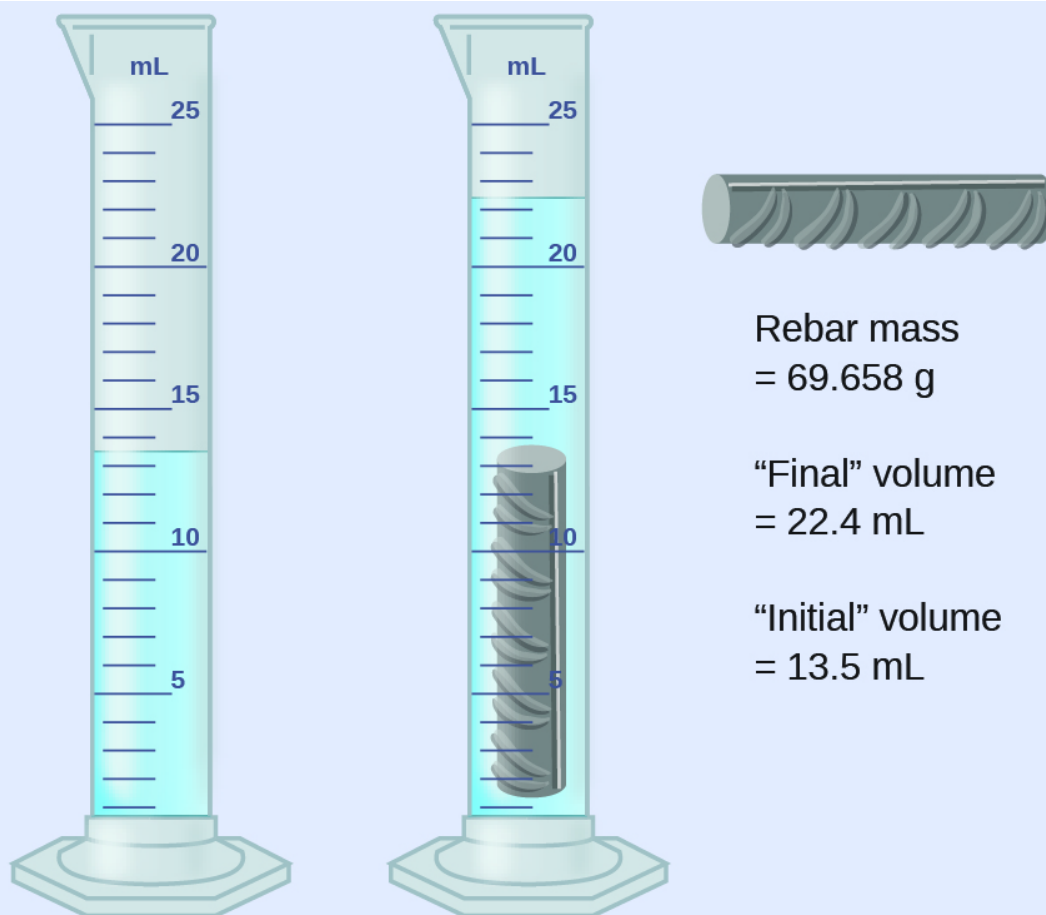
(a) Use these values to determine the density of this piece of rebar.
(b) Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

Equation:

$$\text{volume} = 22.4 \text{ mL} - 13.5 \text{ mL} = 8.9 \text{ mL} = 8.9 \text{ cm}^3$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)
The density is the mass-to-volume ratio:

Equation:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658 \text{ g}}{8.9 \text{ cm}^3} = 7.8 \text{ g/cm}^3$$

(rounded to two significant figures, per the rule for multiplication and division)
From [link], the density of iron is 7.9 g/cm^3, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

Check Your Learning

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.
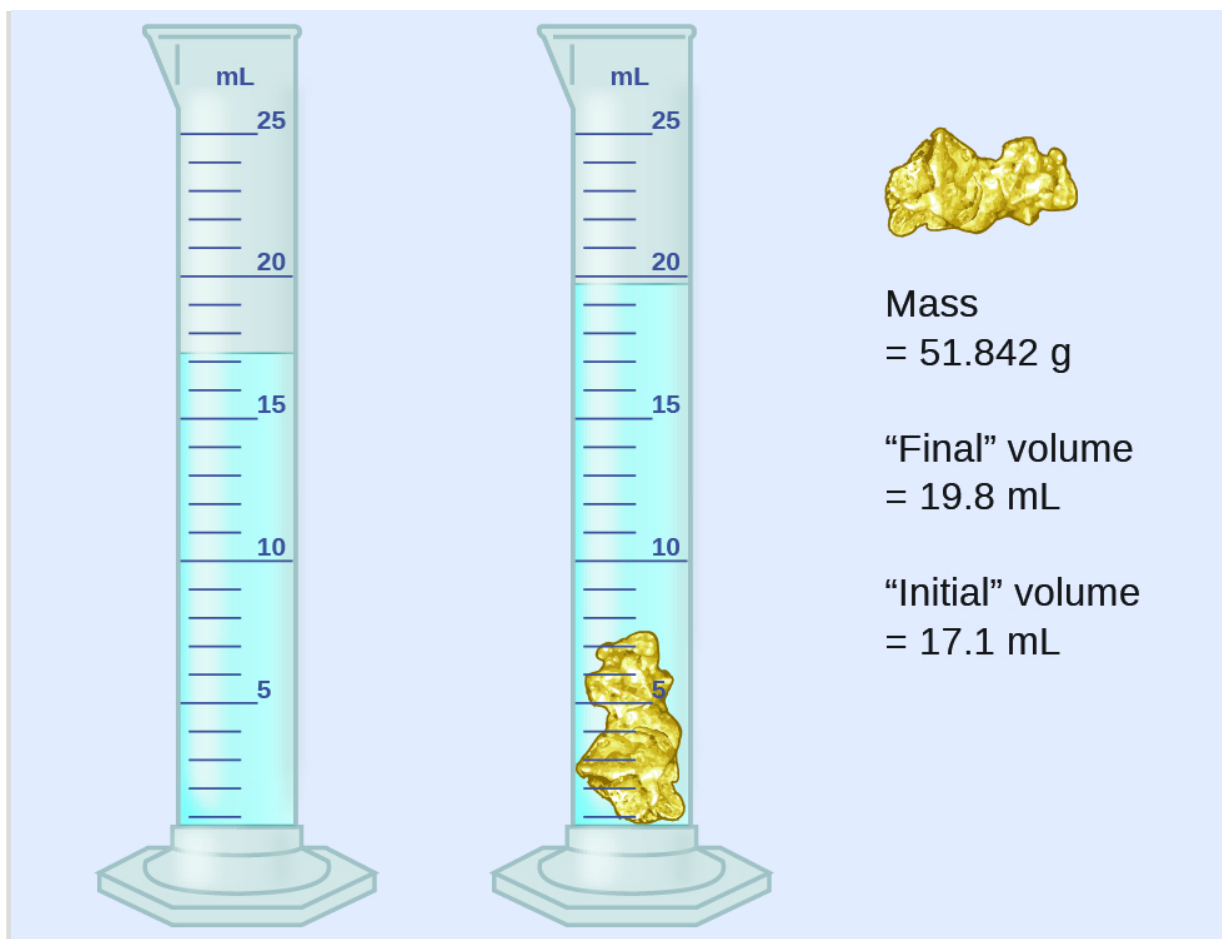
(a) Use these values to determine the density of this material.

(b) Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Note:

Answer:

(a) 19 g/cm^3; (b) It is likely gold; the right appearance for gold and very close to the density given for gold in [link].

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the **precision** and the **accuracy** of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values

agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition ([link]).
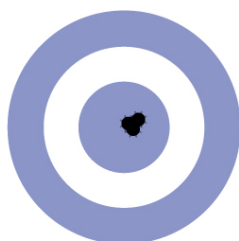
Accurate
and precise

(a)
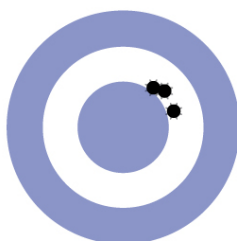
Precise,
not accurate

(b)
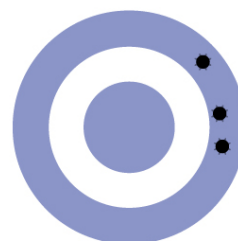
Not accurate,
not precise

(c)

(a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in [link].

Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers		
Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Key Concepts and Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Chemistry End of Chapter Exercises

Exercise:

  Problem:

  Express each of the following numbers in scientific notation with correct significant figures:

  (a) 711.0

  (b) 0.239

  (c) 90743

  (d) 134.2

  (e) 0.05499

  (f) 10000.0

  (g) 0.000000738592

Exercise:

  Problem:

  Express each of the following numbers in exponential notation with correct significant figures:

  (a) 704

  (b) 0.03344

  (c) 547.9

  (d) 22086

(e) 1000.00

(f) 0.0000000651

(g) 0.007157

Solution:

(a) 7.04×10^2; (b) 3.344×10^{-2}; (c) 5.479×10^2; (d) 2.2086×10^4; (e) 1.00000×10^3; (f) 6.51×10^{-8}; (g) 7.157×10^{-3}

Exercise:

Problem:

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

(a) the number of eggs in a basket

(b) the mass of a dozen eggs

(c) the number of gallons of gasoline necessary to fill an automobile gas tank

(d) the number of cm in 2 m

(e) the mass of a textbook

(f) the time required to drive from San Francisco to Kansas City at an average speed of 53 mi/h

Exercise:

Problem:

Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

(a) the number of seconds in an hour

(b) the number of pages in this book

(c) the number of grams in your weight

(d) the number of grams in 3 kilograms

(e) the volume of water you drink in one day

(f) the distance from San Francisco to Kansas City

Solution:

(a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

Exercise:

Problem: How many significant figures are contained in each of the following measurements?

(a) 38.7 g

(b) 2×10^{18} m

(c) 3,486,002 kg

(d) 9.74150×10^{-4} J

(e) 0.0613 cm^3

(f) 17.0 kg

(g) 0.01400 g/mL

Exercise:

Problem: How many significant figures are contained in each of the following measurements?

(a) 53 cm

(b) 2.05×10^8 m

(c) 86,002 J

(d) 9.740×10^4 m/s

(e) 10.0613 m^3

(f) 0.17 g/mL

(g) 0.88400 s

Solution:

(a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

Exercise:

Problem:

The following quantities were reported on the labels of commercial products. Determine the number of significant figures in each.

(a) 0.0055 g active ingredients

(b) 12 tablets

(c) 3% hydrogen peroxide

(d) 5.5 ounces

(e) 473 mL

(f) 1.75% bismuth

(g) 0.001% phosphoric acid

(h) 99.80% inert ingredients

Exercise:

Problem: Round off each of the following numbers to two significant figures:

(a) 0.436

(b) 9.000

(c) 27.2

(d) 135

(e) 1.497×10^{-3}

(f) 0.445

Solution:

(a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3}; (f) 0.44

Exercise:

Problem: Round off each of the following numbers to two significant figures:

(a) 517

(b) 86.3

(c) 6.382×10^3

(d) 5.0008

(e) 22.497

(f) 0.885

Exercise:

Problem:

Perform the following calculations and report each answer with the correct number of significant figures.

(a) 628×342

(b) $(5.63 \times 10^2) \times (7.4 \times 10^3)$

(c) $\frac{28.0}{13.483}$

(d) 8119×0.000023

(e) $14.98 + 27{,}340 + 84.7593$

(f) $42.7 + 0.259$

Solution:

(a) 2.15×10^5; (b) 4.2×10^6; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

Exercise:

Problem:

Perform the following calculations and report each answer with the correct number of significant figures.

(a) 62.8×34

(b) $0.147 + 0.0066 + 0.012$

(c) $38 \times 95 \times 1.792$

(d) $15 - 0.15 - 0.6155$

(e) $8.78 \times \frac{0.0500}{0.478}$

(f) $140 + 7.68 + 0.014$

(g) $28.7 - 0.0483$

(h) $\frac{(88.5 - 87.57)}{45.13}$

Exercise:

Problem: Consider the results of the archery contest shown in this figure.

(a) Which archer is most precise?

(b) Which archer is most accurate?

(c) Who is both least precise and least accurate?

Archer W   Archer X   Archer Y   Archer Z
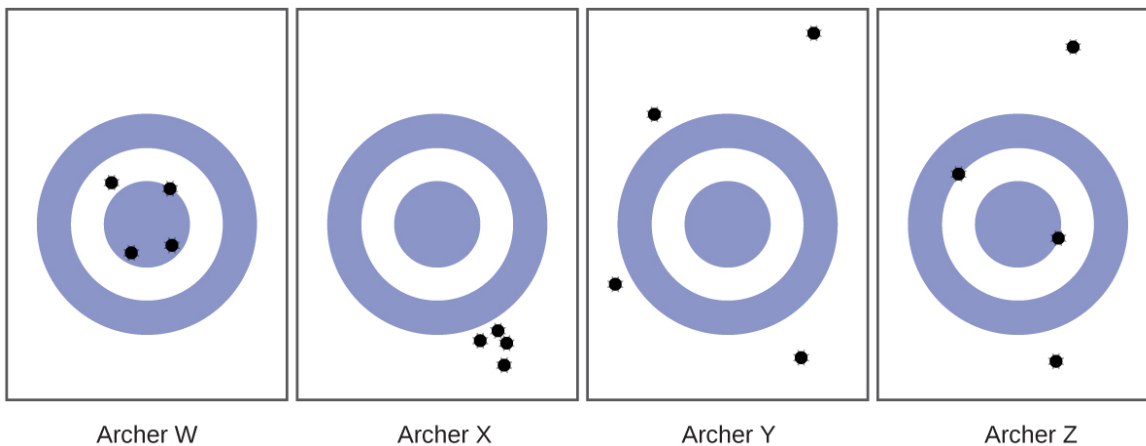
Solution:

(a) Archer X; (b) Archer W; (c) Archer Y

Exercise:

Problem: Classify the following sets of measurements as accurate, precise, both, or neither.

(a) Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g

(b) Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL

Glossary

accuracy
    how closely a measurement aligns with a correct value

exact number
    number derived by counting or by definition

precision
    how closely a measurement matches the same measurement when repeated

rounding
    procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

significant figures
    (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

uncertainty
    estimate of amount by which measurement differs from true value

Mathematical Treatment of Measurement Results
By the end of this section, you will be able to:

- Explain the dimensional analysis (factor label) approach to mathematical calculations involving quantities
- Use dimensional analysis to carry out unit conversions for a given property and computations involving two or more properties

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:
Equation:

$$\text{speed} = \frac{\text{distance}}{\text{time}}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of
Equation:

$$\frac{100 \text{ m}}{10 \text{ s}} = 10 \text{ m/s}$$

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity (100/10 = 10) *and likewise* dividing the units of each measured quantity to yield the unit of the computed quantity (m/s = m/s). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation between the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:
Equation:

$$\text{time} = \frac{\text{distance}}{\text{speed}}$$

The time can then be computed as:
Equation:

$$\frac{25 \text{ m}}{10 \text{ m/s}} = 2.5 \text{ s}$$

Again, arithmetic on the numbers (25/10 = 2.5) was accompanied by the same arithmetic on the units (m/m/s = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is "1"—or, as commonly phrased, the units "cancel."

These calculations are examples of a versatile mathematical approach known as **dimensional analysis** (or the **factor-label method**). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

Conversion Factors and Dimensional Analysis

A ratio of two equivalent quantities expressed with different measurement units can be used as a **unit conversion factor**. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

Equation:

$$\frac{2.54 \text{ cm}}{1 \text{ in.}} \ (2.54 \text{ cm} = 1 \text{ in.}) \text{ or } 2.54 \ \frac{\text{cm}}{\text{in.}}$$

Several other commonly used conversion factors are given in [link].

Common Conversion Factors		
Length	**Volume**	**Mass**
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

When we multiply a quantity (such as distance given in inches) by an appropriate unit conversion factor, we convert the quantity to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

Equation:

$$34 \cancel{\text{ in.}} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{ in.}}} = 86 \text{ cm}$$

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield $\frac{\text{in.} \times \text{cm}}{\text{in.}}$. Just as for numbers, a ratio of identical units is also numerically equal to one, $\frac{\text{in.}}{\text{in.}} = 1$, and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to "cancel.") Using dimensional analysis, we can determine that a unit conversion factor has been set up correctly by checking to confirm that the original unit will cancel, and the result will contain the sought (converted) unit.

Example:

Using a Unit Conversion Factor

The mass of a competition frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g ([link]).

Solution

If we have the conversion factor, we can determine the mass in kilograms using an equation similar the one used for converting length from inches to centimeters.

Equation:

$$x \text{ oz} = 125 \text{ g} \times \text{ unit conversion factor}$$

We write the unit conversion factor in its two forms:
Equation:

$$\frac{1 \text{ oz}}{28.349 \text{ g}} \text{ and } \frac{28.349 \text{ g}}{1 \text{ oz}}$$

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.
Equation:

$$
\begin{aligned}
x \text{ oz} &= 125 \ \cancel{\text{g}} \times \frac{1 \text{ oz}}{28.349 \ \cancel{\text{g}}} \\
&= \left(\frac{125}{28.349}\right) \text{oz} \\
&= 4.41 \text{ oz (three significant figures)}
\end{aligned}
$$

Check Your Learning
Convert a volume of 9.345 qt to liters.

Note:
Answer:
8.844 L

Beyond simple unit conversions, the factor-label method can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to insure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. This is why it is referred to as the factor-label method. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example:
Computing Quantities from Measurement Results and Known Mathematical Relations
What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.
Solution
Since density $= \frac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A × unit conversion factor. The necessary conversion factors are given in [link]: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams in one step:
Equation:

$$9.26 \ \cancel{\text{lb}} \times \frac{453.59 \text{ g}}{1 \ \cancel{\text{lb}}} = 4.20 \times 10^3 \text{ g}$$

We need to use two steps to convert volume from quarts to milliliters.

Convert quarts to liters.   **Equation:**

$$4.00 \ \cancel{\text{qt}} \times \frac{1 \text{ L}}{1.0567 \ \cancel{\text{qt}}} = 3.78 \text{ L}$$

Convert liters to   **Equation:**

milliliters.

$$3.78\ \cancel{L}\ \times\ \frac{1000\ \text{mL}}{1\ \cancel{L}}\ =\ 3.78\ \times\ 10^3\ \text{mL}$$

Then,
Equation:

$$\text{density} =\ \frac{4.20\ \times\ 10^3\ \text{g}}{3.78\ \times\ 10^3\ \text{mL}}\ =\ 1.11\ \text{g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:
Equation:

$$\frac{9.26\ \cancel{lb}}{4.00\ \cancel{qt}}\ \times\ \frac{453.59\ \text{g}}{1\ \cancel{lb}}\ \times\ \frac{1.0567\ \cancel{qt}}{1\ \cancel{L}}\ \times\ \frac{1\ \cancel{L}}{1000\ \text{mL}}\ =\ 1.11\ \text{g/mL}$$

Check Your Learning
What is the volume in liters of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

Note:
Answer:
$2.956\ \times\ 10^{-2}\ \text{L}$

Example:
Computing Quantities from Measurement Results and Known Mathematical Relations
While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.
(a) What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?
(b) If gasoline costs $3.80 per gallon, what was the fuel cost for this trip?
Solution
(a) We first convert distance from kilometers to miles:
Equation:

$$1250\ \text{km}\ \times\ \frac{0.62137\ \text{mi}}{1\ \text{km}}\ =\ 777\ \text{mi}$$

and then convert volume from liters to gallons:
Equation:

$$213\ \cancel{L}\ \times\ \frac{1.0567\ \cancel{qt}}{1\ \cancel{L}}\ \times\ \frac{1\ \text{gal}}{4\ \cancel{qt}}\ =\ 56.3\ \text{gal}$$

Then,
Equation:

$$(\text{average})\ \text{mileage} =\ \frac{777\ \text{mi}}{56.3\ \text{gal}}\ =\ 13.8\ \text{miles/gallon} = 13.8\ \text{mpg}$$

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:
Equation:

$$\frac{1250 \; \cancel{\text{km}}}{213 \; \cancel{\text{L}}} \times \frac{0.62137 \text{ mi}}{1 \; \cancel{\text{km}}} \times \frac{1 \; \cancel{\text{L}}}{1.0567 \; \cancel{\text{qt}}} \times \frac{4 \; \cancel{\text{qt}}}{1 \text{ gal}} = 13.8 \text{ mpg}$$

(b) Using the previously calculated volume in gallons, we find:

Equation:

$$56.3 \text{ gal} \times \frac{\$3.80}{1 \text{ gal}} = \$214$$

Check Your Learning

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

(a) What (average) fuel economy, in miles per gallon, did the Prius get during this trip?

(b) If gasoline costs $3.90 per gallon, what was the fuel cost for this trip?

Note:
Answer:
(a) 51 mpg; (b) $62

Conversion of Temperature Units

We use the word temperature to refer to the hotness or coldness of a substance. One way we measure a change in temperature is to use the fact that most substances expand when their temperature increases and contract when their temperature decreases. The mercury or alcohol in a common glass thermometer changes its volume as the temperature changes. Because the volume of the liquid changes more than the volume of the glass, we can see the liquid expand when it gets warmer and contract when it gets cooler.

To mark a scale on a thermometer, we need a set of reference values: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the **Fahrenheit** scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

Defining the Celsius and Fahrenheit temperature scales as described in the previous paragraph results in a slightly more complex relationship between temperature values on these two scales than for different units of measure for other properties. Most measurement units for a given property are directly proportional to one another (y = mx). Using familiar length units as one example:

Equation:

$$\text{length in feet} = \left(\frac{1 \text{ ft}}{12 \text{ in.}} \right) \times \text{length in inches}$$

where y = length in feet, x = length in inches, and the proportionality constant, m, is the conversion factor. The Celsius and Fahrenheit temperature scales, however, do not share a common zero point, and so the relationship between these two scales is a linear one rather than a proportional one (y = mx + b). Consequently, converting a temperature from one of these scales into the other requires more than simple multiplication by a conversion factor, m, it also must take into account differences in the scales' zero points (b).

The linear equation relating Celsius and Fahrenheit temperatures is easily derived from the two temperatures used to define each scale. Representing the Celsius temperature as x and the Fahrenheit temperature as y, the slope, m, is computed to be:

Equation:

$$m = \frac{\Delta y}{\Delta x} = \frac{212\ ^\circ\mathrm{F} - 32\ ^\circ\mathrm{F}}{100\ ^\circ\mathrm{C} - 0\ ^\circ\mathrm{C}} = \frac{180\ ^\circ\mathrm{F}}{100\ ^\circ\mathrm{C}} = \frac{9\ ^\circ\mathrm{F}}{5\ ^\circ\mathrm{C}}$$

The y-intercept of the equation, b, is then calculated using either of the equivalent temperature pairs, (100 °C, 212 °F) or (0 °C, 32 °F), as:

Equation:

$$b = y - mx = 32\ ^\circ\mathrm{F} - \frac{9\ ^\circ\mathrm{F}}{5\ ^\circ\mathrm{C}} \times 0\ ^\circ\mathrm{C} = 32\ ^\circ\mathrm{F}$$

The equation relating the temperature scales is then:

Equation:

$$T_{^\circ\mathrm{F}} = \left(\frac{9\ ^\circ\mathrm{F}}{5\ ^\circ\mathrm{C}} \times T_{^\circ\mathrm{C}} \right) + 32\ ^\circ\mathrm{C}$$

An abbreviated form of this equation that omits the measurement units is:

Equation:

$$T_{^\circ\mathrm{F}} = \frac{9}{5} \times T_{^\circ\mathrm{C}} + 32$$

Rearrangement of this equation yields the form useful for converting from Fahrenheit to Celsius:

Equation:

$$T_{^\circ\mathrm{C}} = \frac{5}{9} (T_{^\circ\mathrm{F}} - 32)$$

As mentioned earlier in this chapter, the SI unit of temperature is the kelvin (K). Unlike the Celsius and Fahrenheit scales, the kelvin scale is an absolute temperature scale in which 0 (zero) K corresponds to the lowest temperature that can theoretically be achieved. The early 19th-century discovery of the relationship between a gas's volume and temperature suggested that the volume of a gas would be zero at −273.15 °C. In 1848, British physicist William Thompson, who later adopted the title of Lord Kelvin, proposed an absolute temperature scale based on this concept (further treatment of this topic is provided in this text's chapter on gases).

The freezing temperature of water on this scale is 273.15 K and its boiling temperature 373.15 K. Notice the numerical difference in these two reference temperatures is 100, the same as for the Celsius scale, and so the linear relation between these two temperature scales will exhibit a slope of $1\ \frac{\mathrm{K}}{^\circ\mathrm{C}}$. Following the same approach, the equations for converting between the kelvin and Celsius temperature scales are derived to be:

Equation:

$$T_{\mathrm{K}} = T_{^\circ\mathrm{C}} + 273.15$$

Equation:

$$T_{^\circ\mathrm{C}} = T_{\mathrm{K}} - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. [link] shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.
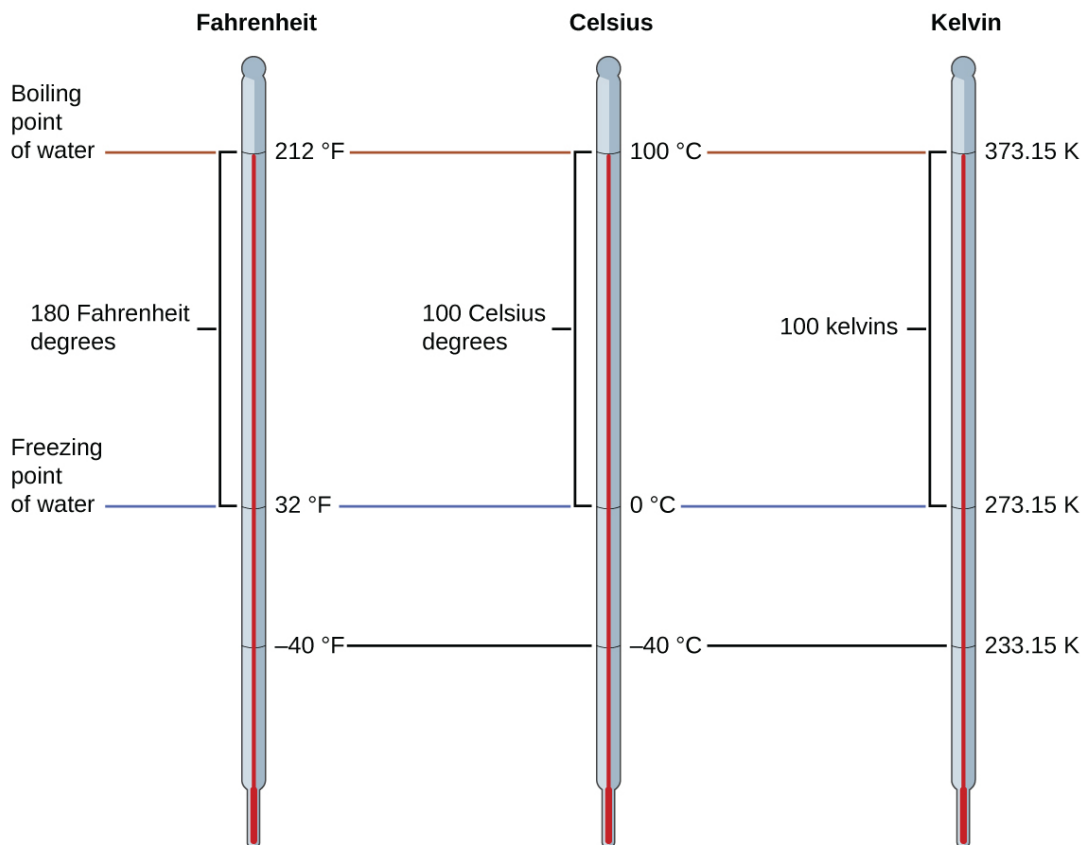
The Fahrenheit, Celsius, and kelvin temperature scales are compared.

Although the kelvin (absolute) temperature scale is the official SI temperature scale, Celsius is commonly used in many scientific contexts and is the scale of choice for nonscience contexts in almost all areas of the world. Very few countries (the U.S. and its territories, the Bahamas, Belize, Cayman Islands, and Palau) still use Fahrenheit for weather, medicine, and cooking.

Example:
Conversion from Celsius
Normal body temperature has been commonly accepted as 37.0 °C (although it varies depending on time of day and method of measurement, as well as among individuals). What is this temperature on the kelvin scale and on the Fahrenheit scale?
Solution
Equation:

$$\text{K} = {}^\circ\text{C} + 273.15 = 37.0 + 273.2 = 310.2 \text{ K}$$

Equation:

$$°F = \frac{9}{5}°C + 32.0 = \left(\frac{9}{5} \times 37.0\right) + 32.0 = 66.6 + 32.0 = 98.6 °F$$

Check Your Learning
Convert 80.92 °C to K and °F.

Note:
Answer:
354.07 K, 177.7 °F

Example:
Conversion from Fahrenheit
Baking a ready-made pizza calls for an oven temperature of 450 °F. If you are in Europe, and your oven thermometer uses the Celsius scale, what is the setting? What is the kelvin temperature?
Solution
Equation:

$$°C = \frac{5}{9}(°F - 32) = \frac{5}{9}(450 - 32) = \frac{5}{9} \times 418 = 232 °C \longrightarrow \text{set oven to } 230 °C \qquad \text{(two signific}$$

Equation:

$$K = °C + 273.15 = 230 + 273 = 503 \text{ K} \longrightarrow 5.0 \times 10^2 K \qquad \text{(two significant figures)}$$

Check Your Learning
Convert 50 °F to °C and K.

Note:
Answer:
10 °C, 280 K

Key Concepts and Summary

Measurements are made using a variety of units. It is often useful or necessary to convert a measured quantity from one unit into another. These conversions are accomplished using unit conversion factors, which are derived by simple applications of a mathematical approach called the factor-label method or dimensional analysis. This strategy is also employed to calculate sought quantities using measured quantities and appropriate mathematical relations.

Key Equations

- $T_{°C} = \frac{5}{9} \times T_{°F} - 32$
- $T_{°F} = \frac{9}{5} \times T_{°C} + 32$

- $T_K = {}^\circ C + 273.15$
- $T_{{}^\circ C} = K - 273.15$

Chemistry End of Chapter Exercises

Exercise:

Problem: Write conversion factors (as ratios) for the number of:

(a) yards in 1 meter

(b) liters in 1 liquid quart

(c) pounds in 1 kilogram

Solution:

(a) $\frac{1.0936\ yd}{1\ m}$; (b) $\frac{0.94635\ L}{1\ qt}$; (c) $\frac{2.2046\ lb}{1\ kg}$

Exercise:

Problem: Write conversion factors (as ratios) for the number of:

(a) kilometers in 1 mile

(b) liters in 1 cubic foot

(c) grams in 1 ounce

Exercise:

Problem:

The label on a soft drink bottle gives the volume in two units: 2.0 L and 67.6 fl oz. Use this information to derive a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

Solution:

$\frac{2.0\ L}{67.6\ fl\ oz} = \frac{0.030\ L}{1\ fl\ oz}$

Only two significant figures are justified.

Exercise:

Problem:

The label on a box of cereal gives the mass of cereal in two units: 978 grams and 34.5 oz. Use this information to find a conversion factor between the English and metric units. How many significant figures can you justify in your conversion factor?

Exercise:

Problem:

Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimeters and grams?

Solution:

68–71 cm; 400–450 g

Exercise:

Problem:

A woman's basketball has a circumference between 28.5 and 29.0 inches and a maximum weight of 20 ounces (two significant figures). What are these specifications in units of centimeters and grams?

Exercise:

Problem: How many milliliters of a soft drink are contained in a 12.0-oz can?

Solution:

355 mL

Exercise:

Problem: A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?

Exercise:

Problem: The diameter of a red blood cell is about 3×10^{-4} in. What is its diameter in centimeters?

Solution:

8×10^{-4} cm

Exercise:

Problem:

The distance between the centers of the two oxygen atoms in an oxygen molecule is 1.21×10^{-8} cm. What is this distance in inches?

Exercise:

Problem: Is a 197-lb weight lifter light enough to compete in a class limited to those weighing 90 kg or less?

Solution:

yes; weight = 89.4 kg

Exercise:

Problem:

A very good 197-lb weight lifter lifted 192 kg in a move called the clean and jerk. What was the mass of the weight lifted in pounds?

Exercise:

Problem: Many medical laboratory tests are run using 5.0 μL blood serum. What is this volume in milliliters?

Solution:

5.0×10^{-3} mL

Exercise:

Problem: If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?

Exercise:

Problem:

Use scientific (exponential) notation to express the following quantities in terms of the SI base units in [link]:

(a) 0.13 g

(b) 232 Gg

(c) 5.23 pm

(d) 86.3 mg

(e) 37.6 cm

(f) 54 μm

(g) 1 Ts

(h) 27 ps

(i) 0.15 mK

Solution:

(a) 1.3×10^{-4} kg; (b) 2.32×10^{8} kg; (c) 5.23×10^{-12} m; (d) 8.63×10^{-5} kg; (e) 3.76×10^{-1} m; (f) 5.4×10^{-5} m; (g) 1×10^{12} s; (h) 2.7×10^{-11} s; (i) 1.5×10^{-4} K

Exercise:

Problem: Complete the following conversions between SI units.

(a) 612 g = _____ mg

(b) 8.160 m = _____ cm

(c) 3779 μg = _____ g

(d) 781 mL = _____ L

(e) 4.18 kg = _____ g

(f) 27.8 m = _____ km

(g) 0.13 mL = _____ L

(h) 1738 km = _____ m

Exercise:

Problem:

Gasoline is sold by the liter in many countries. How many liters are required to fill a 12.0-gal gas tank?

Solution:

45.4 L

Exercise:

Problem: Milk is sold by the liter in many countries. What is the volume of exactly 1/2 gal of milk in liters?

Exercise:

Problem: A long ton is defined as exactly 2240 lb. What is this mass in kilograms?

Solution:

1.0160×10^3 kg

Exercise:

Problem: Make the conversion indicated in each of the following:

(b) the greatest depth of the ocean, about 6.5 mi, to kilometers

(c) the area of the state of Oregon, 96,981 mi², to square kilometers

(d) the volume of 1 gill (exactly 4 oz) to milliliters

(f) the mass of a 3525-lb car to kilograms

(g) the mass of a 2.3-oz egg to grams

Exercise:

Problem: Make the conversion indicated in each of the following:

(a) the length of a soccer field, 120 m (three significant figures), to feet

(b) the height of Mt. Kilimanjaro, at 19,565 ft the highest mountain in Africa, to kilometers

(c) the area of an 8.5 t 11-inch sheet of paper in cm²

(d) the estimated mass of the atmosphere, 5.6 t 10^{15} tons, to kilograms

(e) the mass of a bushel of rye, 32.0 lb, to kilograms

(f) the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)

Solution:

(a) 394 ft
(b) 5.9634 km
(c) 6.0×10^2
(d) 5.1×10^{18} kg
(e) 14.5 kg
(f) 324 mg

Exercise:

Problem:

As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?

Solution:

Yes, the acid's volume is 123 mL.

Exercise:

Problem:

A chemistry student is 159 cm tall and weighs 45.8 kg. What is her height in inches and weight in pounds?

Solution:

62.6 in (about 5 ft 3 in.) and 101 lb

Exercise:

Problem: Calculate the density of aluminum if 27.6 cm^3 has a mass of 74.6 g.

Solution:

2.70 g/cm^3

Exercise:

Problem:

Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm^3?

Exercise:

Problem: Calculate these masses.

(a) What is the mass of 6.00 cm^3 of mercury, density = 13.5939 g/cm^3?

(b) What is the mass of 25.0 mL octane, density = 0.702 g/cm^3?

Solution:

(a) 81.6 g; (b) 17.6 g

Exercise:

Problem: Calculate these masses.

(a) What is the mass of 4.00 cm^3 of sodium, density = 0.97 g/cm^3 ?

(b) What is the mass of 125 mL gaseous chlorine, density = 3.16 g/L?

Exercise:

Problem: Calculate these volumes.

(a) What is the volume of 25 g iodine, density = 4.93 g/cm^3?

(b) What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

Solution:

(a) 5.1 mL; (b) 37 L

Exercise:

Problem: Calculate these volumes.

(a) What is the volume of 11.3 g graphite, density = 2.25 g/cm^3?

(b) What is the volume of 39.657 g bromine, density = 2.928 g/cm^3?

Exercise:

Problem: Convert the temperature of the coldest area in a freezer, −10 °F, to degrees Celsius and kelvin.

Solution:

−23 °C, 250 K

Exercise:

Problem:

The weather in Europe was unusually warm during the summer of 1995. The TV news reported temperatures as high as 45 °C. What was the temperature on the Fahrenheit scale?

Solution:

113 °F

Glossary

dimensional analysis
    (also, factor-label method) versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Fahrenheit
    unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

unit conversion factor
    ratio of equivalent quantities expressed with different units; used to convert from one unit to a different unit

Formula Mass and the Mole Concept
By the end of this section, you will be able to:

- Calculate formula masses for covalent and ionic compounds
- Define the amount unit mole and the related quantity Avogadro's number Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.
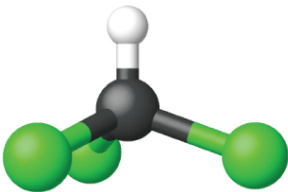
Formula Mass

In an earlier chapter, we described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the **formula mass** of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. [link] outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.
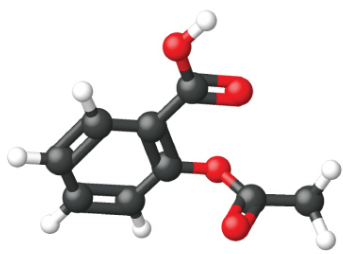
Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
			Molecular mass		119.37

The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu ([link]).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
			Molecular mass		180.15

The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$.
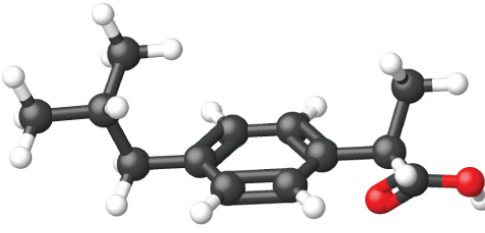
Example:
Computing Molecular Mass for a Covalent Compound
Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?
Solution
Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
			Molecular mass		206.27

Check Your Learning

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Note:
Answer:
151.16 amu

Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass."

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (see [link]).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
			Formula mass		58.44
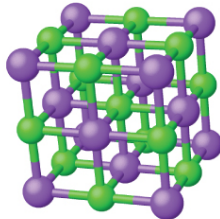
Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.
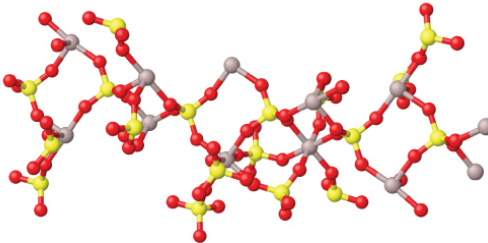
Example:
Computing Formula Mass for an Ionic Compound
Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?
Solution
The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
			Molecular mass		342.14

The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A **mole** is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word "mole" is "large mass" or "bulk," which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named **Avogadro's number (N_A)** or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of "per mole," a conveniently rounded version being 6.022×10^{23}/mol.

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The

molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see [link]).
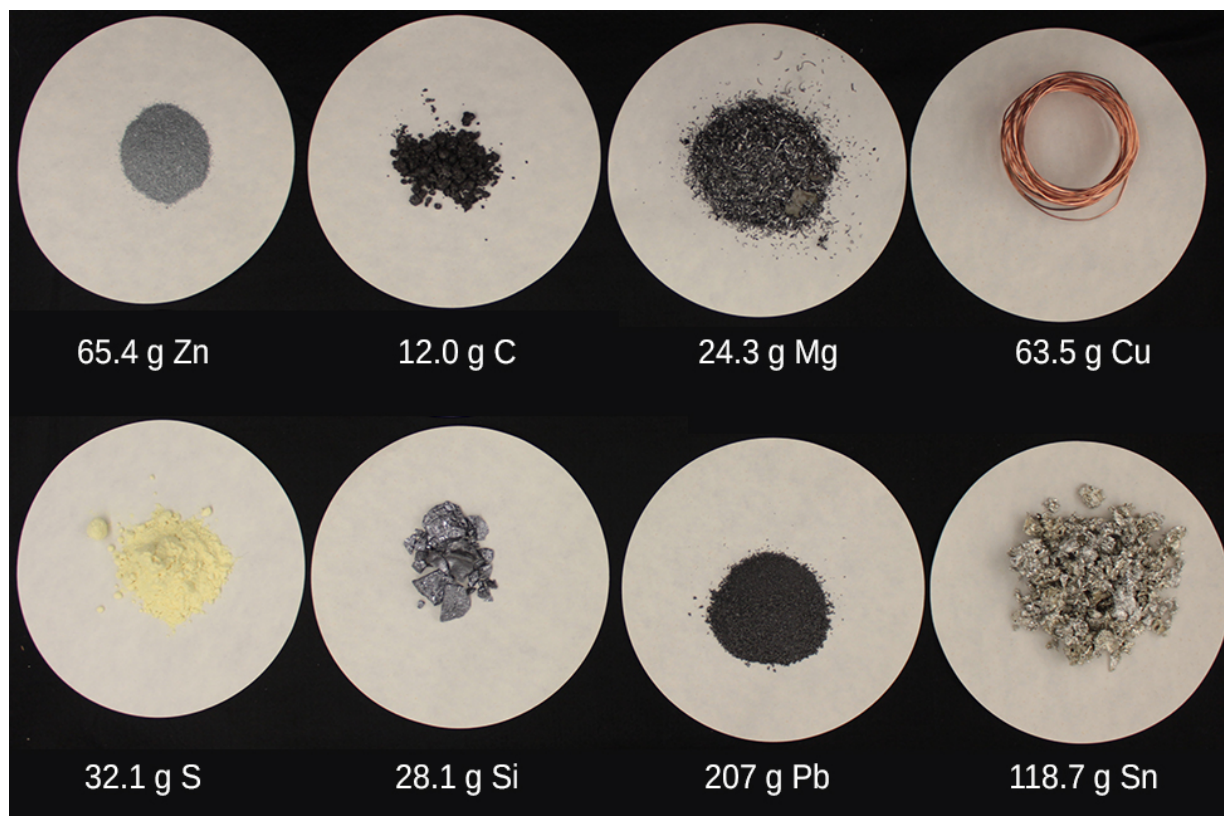
Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu ([link]).

Each sample contains 6.02×10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022×10^{23}
H	1.008	1.008	6.022×10^{23}
O	16.00	16.00	6.022×10^{23}

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
Na	22.99	22.99	6.022×10^{23}
Cl	35.45	33.45	6.022×10^{23}

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see [link]). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.
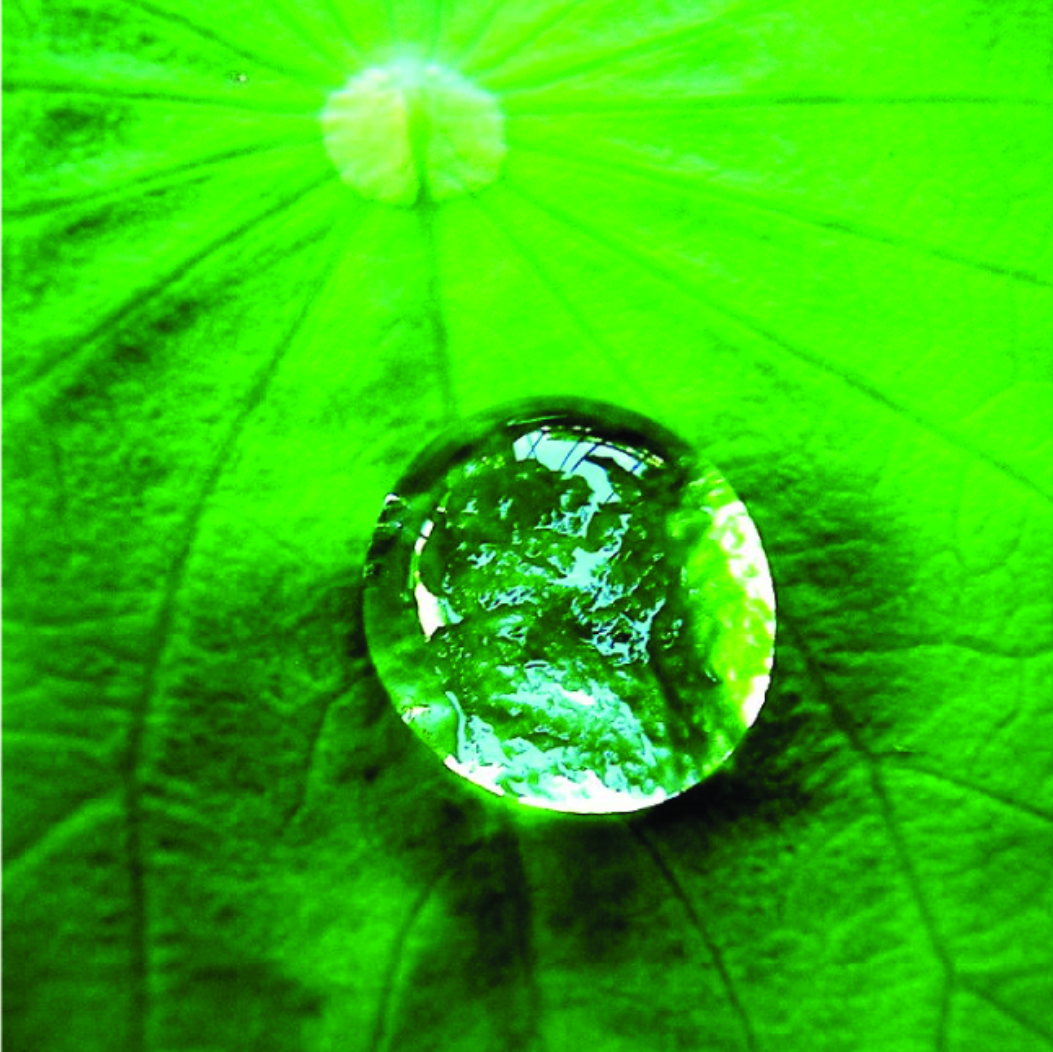
The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: "tanakawho"/Wikimedia commons)

Note:

The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this <u>video</u> and then complete the "Think" questions that follow. Explore more about the mole by reviewing the information under "Dig Deeper."

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

Example:
Deriving Moles from Grams for an Element
According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?
Solution
The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.
The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):
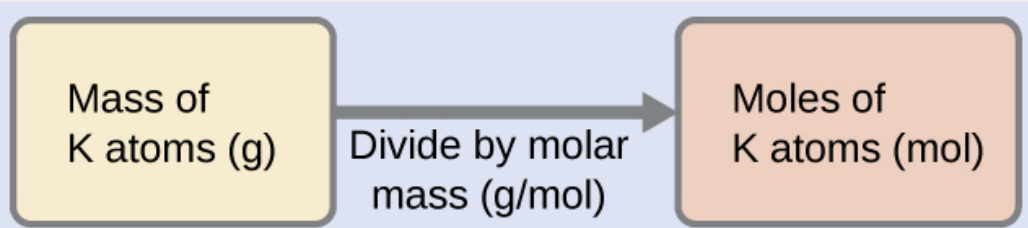
The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"
Equation:

$$4.7 \, \cancel{g} \, K \left(\frac{\text{mol K}}{39.10 \, \cancel{g}} \right) = 0.12 \, \text{mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

Example:
Deriving Grams from Moles for an Element
A liter of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a liter of air?
Solution
The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth ($\sim 10^{-3}$) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~ 0.04 g):
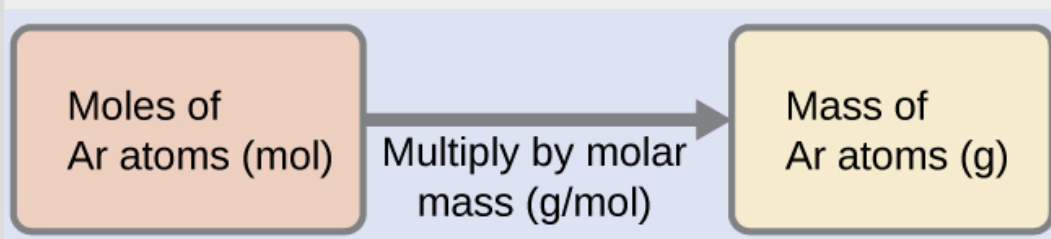
In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):
Equation:

$$9.2 \times 10^{-4} \, \cancel{\text{mol}} \, \text{Ar} \left(\frac{39.95 \text{ g}}{\cancel{\text{mol}} \, \text{Ar}} \right) = 0.037 \text{ g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.
Check Your Learning
What is the mass of 2.561 mol of gold?

Note:
Answer:

504.4 g

Example:
Deriving Number of Atoms from Mass for an Element
Copper is commonly used to fabricate electrical wire ([link]). How many copper atoms are in 5.00 g of copper wire?
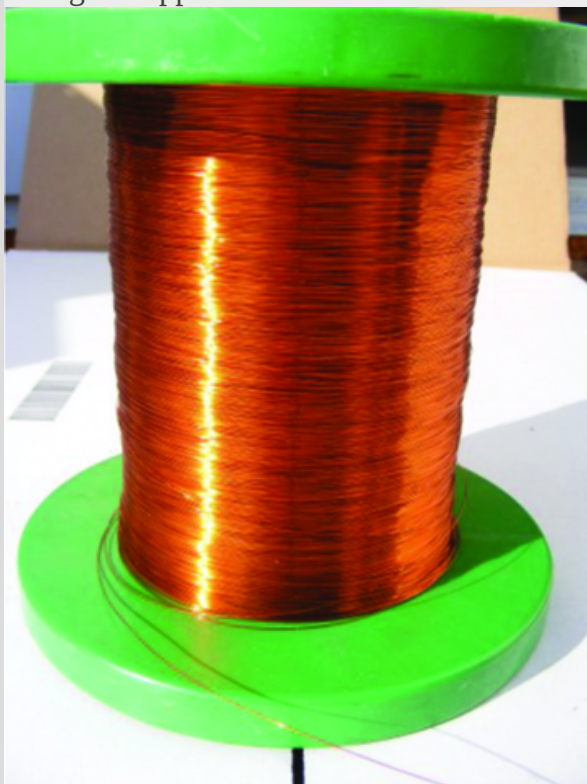
Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution
The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:
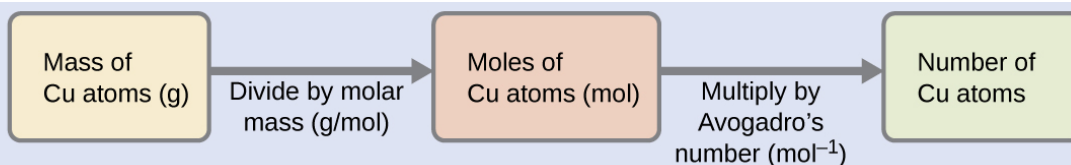
Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

Equation:

$$5.00 \; \cancel{\text{g}} \; \text{Cu} \left(\frac{\cancel{\text{mol}} \; \text{Cu}}{63.55 \; \cancel{\text{g}}} \right) \left(\frac{6.022 \times 10^{23} \; \text{atoms}}{\cancel{\text{mol}}} \right) = 4.74 \times 10^{22} \text{atoms of copper}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

Check Your Learning

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Note:
Answer:
4.586×10^{22} Au atoms

Example:
Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in [link]:
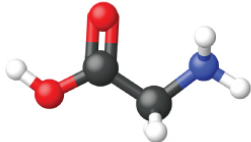
The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
	Molecular mass (g/mol compound)				75.07

The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

Equation:

$$28.35 \, \cancel{g} \, \text{glycine} \left(\frac{\text{mol glycine}}{75.07 \, \cancel{g}} \right) = 0.378 \, \text{mol glycine}$$

This result is consistent with our rough estimate.

Check Your Learning

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Note:
Answer:
0.073 mol

Example:
Deriving Grams from Moles for a Compound
Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?
Solution
As for elements, the mass of a compound can be derived from its molar amount as shown:
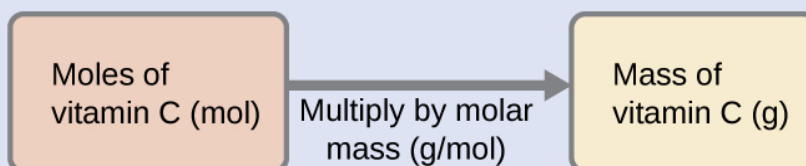
The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole ($\sim10^{-4}$ or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass ($\sim$0.02 g). Performing the calculation, we get:
Equation:

$$1.42 \times 10^{-4} \; \cancel{\text{mol}} \; \text{vitamin C} \left(\frac{176.124 \, \text{g}}{\cancel{\text{mol}} \, \text{vitamin C}} \right) = 0.0250 \, \text{g vitamin C}$$

This is consistent with the anticipated result.
Check Your Learning
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Note:
Answer:
14.2 g

Example:
Deriving the Number of Atoms and Molecules from the Mass of a Compound
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:
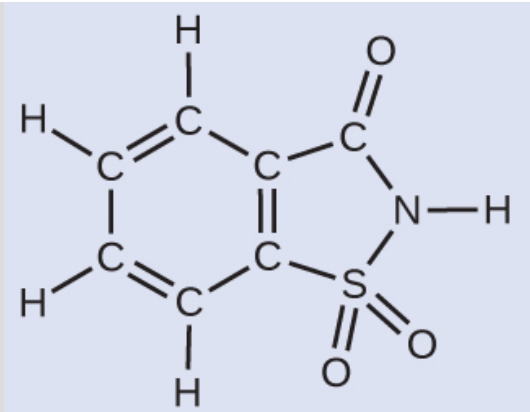
Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in [link], and then multiplying by Avogadro's number:
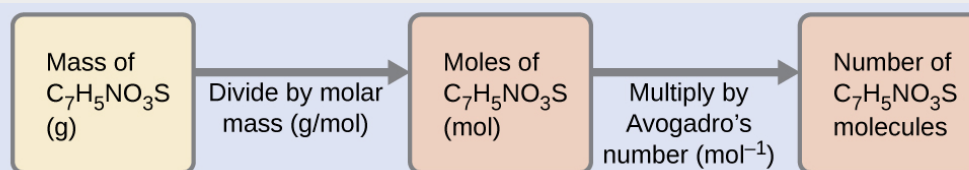
Using the provided mass and molar mass for saccharin yields:

Equation:

$$0.0400 \; \cancel{g} \; C_7H_5NO_3S \left(\frac{\text{mol} \; C_7H_5NO_3S}{183.18 \; \cancel{g} \; C_7H_5NO_3S} \right) \left(\frac{6.022 \times 10^{23} \; C_7H_5NO_3S \; \text{molecules}}{1 \; \text{mol} \; C_7H_5NO_3S} \right)$$

$$= 1.31 \times 10^{20} \; C_7H_5NO_3S \; \text{molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

Equation:

$$1.31 \times 10^{20} \; C_7H_5NO_3S \; \text{molecules} \left(\frac{7 \; \text{C atoms}}{1 \; C_7H_5NO_3S \; \text{molecule}} \right) = 9.20 \times 10^{21} \; \text{C atoms}$$

Check Your Learning

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Note:

Answer:
9.545×10^{22} molecules $C_4 H_{10}$; 9.545×10^{23} atoms H

Note:

Counting Neurotransmitter Molecules in the Brain

The brain is the control center of the central nervous system ([link]). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions; it processes stimuli detected by sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these advances through the concerted efforts of various industrial, academic, and government agencies (more details available at www.whitehouse.gov/share/brain-initiative).
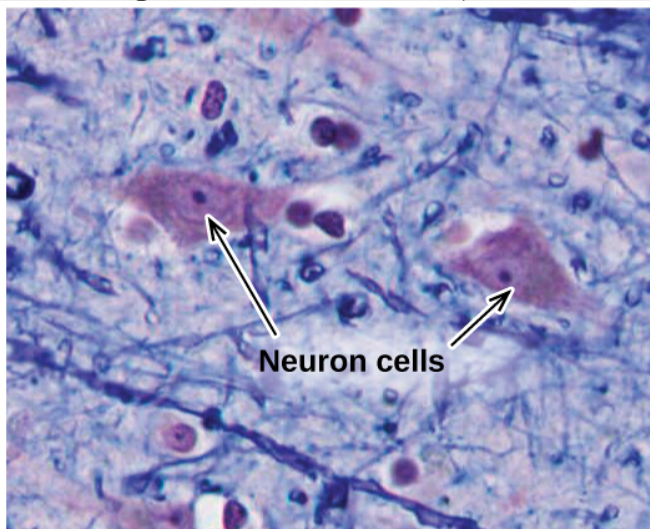
(a)   (b)

(a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse)

and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell wall and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see [link]). One neurotransmitter that has been very extensively studied is dopamine, $C_8H_{11}NO_2$. Dopamine is involved in various neurological processes that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.
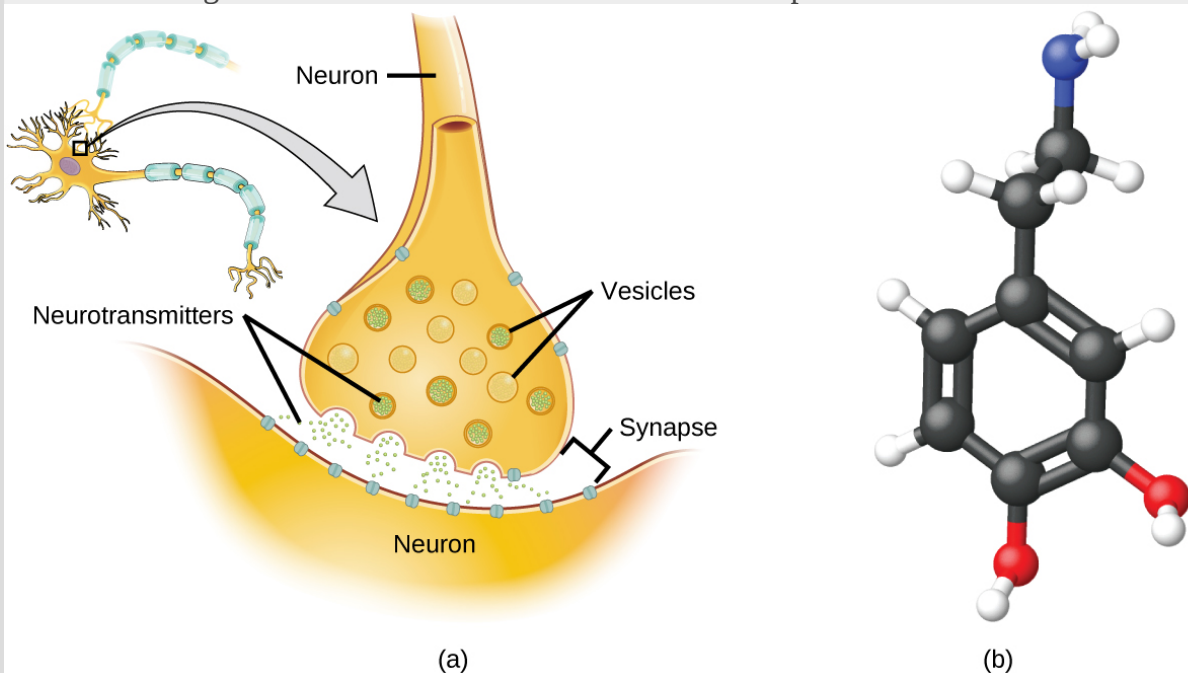
(a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine, $C_8H_{11}NO_2$, is a neurotransmitter involved in a number of neurological processes.

One important aspect of the complex processes related to dopamine signaling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.
Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle

(about 5×10^{-20} mol or 50 zmol). Analysis of these neurons from mice subjected to various drug therapies shows significant changes in the average number of dopamine molecules contained in individual vesicles, increasing or decreasing by up to three-fold, depending on the specific drug used. These studies also indicate that not all of the dopamine in a given vesicle is released during exocytosis, suggesting that it may be possible to regulate the fraction released using pharmaceutical therapies.[footnote]
Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

Key Concepts and Summary

The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molecular mass. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be 6.022×10^{23}, a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

Chemistry End of Chapter Exercises

Exercise:

Problem: What is the total mass (amu) of carbon in each of the following molecules?

(a) CH_4

(b) $CHCl_3$

(c) $C_{12}H_{10}O_6$

(d) $CH_3CH_2CH_2CH_2CH_3$

Solution:

(a) 12.01 amu; (b) 12.01 amu; (c) 144.12 amu; (d) 60.05 amu

Exercise:

Problem: What is the total mass of hydrogen in each of the molecules?

(a) CH_4

(b) $CHCl_3$

(c) $C_{12}H_{10}O_6$

(d) $CH_3CH_2CH_2CH_2CH_3$

Exercise:

Problem: Calculate the molecular or formula mass of each of the following:

(a) P_4

(b) H_2O

(c) $Ca(NO_3)_2$

(d) CH_3CO_2H (acetic acid)

(e) $C_{12}H_{22}O_{11}$ (sucrose, cane sugar).

Solution:

(a) 123.896 amu; (b) 18.015 amu; (c) 164.086 amu; (d) 60.052 amu; (e) 342.297 amu

Exercise:

Problem: Determine the molecular mass of the following compounds:
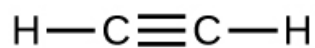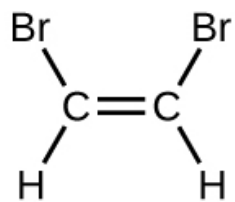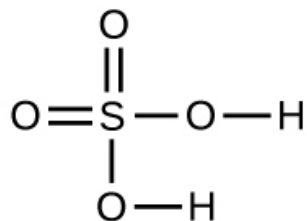
(a)

(b)

(c)

(d)

Exercise:

Problem: Determine the molecular mass of the following compounds:

(a)

(b)

(c)

(d)

$$O{=}\overset{\displaystyle \overset{O-H}{|}}{\underset{\displaystyle \underset{O-H}{|}}{P}}{-}O{-}H$$
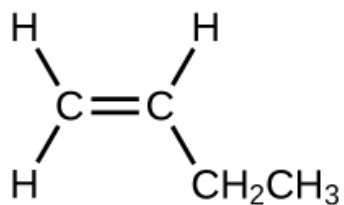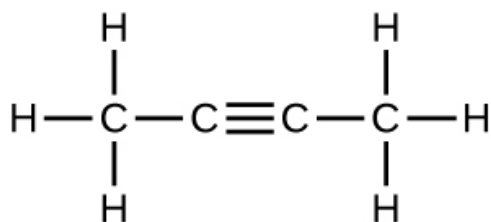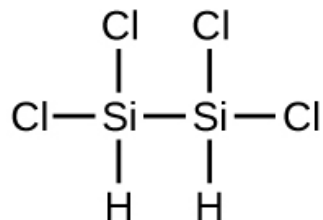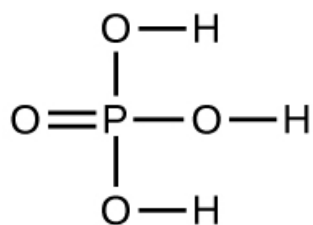
Solution:

(a) 56.107 amu;
(b) 54.091 amu;
(c) 199.9976 amu;
(d) 97.9950 amu

Exercise:

Problem: Which molecule has a molecular mass of 28.05 amu?

(a)

$$H-C\equiv C-H$$
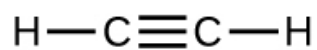
(b)

(c)
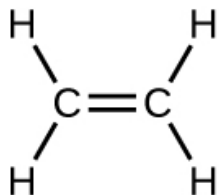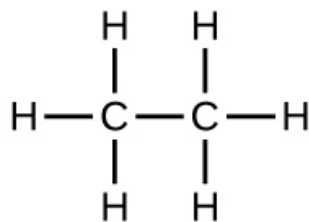
Exercise:

Problem:

Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

Solution:

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

Exercise:

Problem: Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

(a) Which has the largest number of molecules? Explain why.

(b) Which has the greatest mass? Explain why.

Exercise:

Problem:

How are the molecular mass and the molar mass of a compound similar and how are they different?

Solution:

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

Exercise:

Problem: Calculate the molar mass of each of the following compounds:

(a) hydrogen fluoride, HF

(b) ammonia, NH_3

(c) nitric acid, HNO_3

(d) silver sulfate, Ag_2SO_4

(e) boric acid, $B(OH)_3$

Exercise:

Problem: Calculate the molar mass of each of the following:

(a) S_8

(b) C_5H_{12}

(c) $Sc_2(SO_4)_3$

(d) CH_3COCH_3 (acetone)

(e) $C_6H_{12}O_6$ (glucose)

Solution:

(a) 256.528 g/mol; (b) 72.150 g mol^{-1}; (c) 378.103 g mol^{-1}; (d) 58.080 g mol^{-1}; (e) 180.158 g mol^{-1}

Exercise:

Problem: Calculate the molar mass of each of the following:

(a) the anesthetic halothane, $C_2HBrClF_3$

(b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$

(c) caffeine, $C_8H_{10}N_4O_2$

(d) urea, $CO(NH_2)_2$

(e) a typical soap, $C_{17}H_{35}CO_2Na$

Solution:

(a) 197.382 g mol^{-1}; (b) 257.163 g mol^{-1}; (c) 194.193 g mol^{-1}; (d) 60.056 g mol^{-1}; (e) 306.464 g mol^{-1}

Exercise:

Problem:

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

(a) 25.0 g of propylene, C_3H_6

(b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$

(d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$

(e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

Exercise:

Problem: Determine the mass of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) 1.6×10^{-3} mol $Na_2\,SO_4$

(d) 6.854×10^3 mol glucose, $C_6\,H_{12}\,O_6$

(e) 2.86 mol $Co(NH_3)_6Cl_3$

Solution:

(a) 0.819 g;
(b) 307 g;
(c) 0.23 g;
(d) 1.235×10^6 g (1235 kg);
(e) 765 g

Exercise:

Problem:

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

(a) 2.12 g of potassium bromide, KBr

(b) 0.1488 g of phosphoric acid, H_3PO_4

(c) 23 kg of calcium carbonate, $CaCO_3$

(d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$

(e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

Exercise:

Problem: Determine the mass of each of the following:

(a) 2.345 mol LiCl

(b) 0.0872 mol acetylene, C_2H_2

(c) 3.3×10^{-2} mol $Na_2\,CO_3$

(d) 1.23×10^3 mol fructose, $C_6\,H_{12}\,O_6$

(e) 0.5758 mol $FeSO_4(H_2O)_7$

Solution:

(a) 99.41 g;
(b) 2.27 g;
(c) 3.5 g;
(d) 222 kg;
(e) 160.1 g

Exercise:

Problem:

The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, is 1.1 g. What is this requirement in moles?

Exercise:

Problem: Determine the mass in grams of each of the following:

(a) 0.600 mol of oxygen atoms

(b) 0.600 mol of oxygen molecules, O_2

(c) 0.600 mol of ozone molecules, O_3

Solution:

(a) 9.60 g; (b) 19.2 g; (c) 28.8 g

Exercise:

Problem:

A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?

Exercise:

Problem:

Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?

Exercise:

Problem:

One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

Exercise:

Problem:

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

Solution:

0.865 servings, or about 1 serving.

Glossary

Avogadro's number (N_A)
    experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} mol^{-1}

formula mass
    sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

molar mass
    mass in grams of 1 mole of a substance

mole
    amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

Molarity
By the end of this section, you will be able to:

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (see [link]). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.

Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

Solutions

We have previously defined solutions as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce some of the basic properties of solutions.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the **solvent** and may be viewed as the medium in which the other components are dispersed, or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an **aqueous solution**.

A **solute** is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity (*M*)** is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:
Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Example:
Calculating Molar Concentrations
A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133 \text{ mol}}{355 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.375 \, M$$

Check Your Learning

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Note:
Answer:
$0.05 \, M$

Example:
Deriving Moles and Volumes from Molar Concentrations
How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from [link]?

Solution
In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in [link], 0.375 M:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$
$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 0.375 \, \frac{\text{mol sugar}}{\text{L}} \times \left(10 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.004 \text{ mol sugar}$$

Check Your Learning

What volume (mL) of the sweetened tea described in [link] contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Note:
Answer:
80 mL

Example:
Calculating Molar Concentrations from the Mass of Solute
Distilled white vinegar ([link]) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?

Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute's molar mass to obtain the amount of solute in moles:

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2 \text{ g CH}_3\text{CO}_2\text{H} \times \frac{1 \text{ mol CH}_2\text{CO}_2\text{H}}{60.052 \text{ g CH}_2\text{CO}_2\text{H}}}{0.500 \text{ L solution}} = 0.839 \, M$$

Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839\ M$$

$$M = \frac{0.839\ \text{mol solute}}{1.00\ \text{L solution}}$$

Check Your Learning
Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Note:
Answer:
0.674 M

Example:
Determining the Mass of Solute in a Given Volume of Solution
How many grams of NaCl are contained in 0.250 L of a 5.30-M solution?
Solution
The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in [link]:
Equation:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M\ \times\ \text{L solution}$$

$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}}\ \times\ 0.250\ \text{L} = 1.325\ \text{mol NaCl}$$

Finally, this molar amount is used to derive the mass of NaCl:
Equation:

$$1.325\ \text{mol NaCl}\ \times\ \frac{58.44\ \text{g NaCl}}{\text{mol NaCl}} = 77.4\ \text{g NaCl}$$

Check Your Learning
How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

When performing calculations stepwise, as in [link], it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In [link], the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (see [link]). This eliminates intermediate steps so that only the final result is rounded.

Example:
Determining the Volume of Solution Containing a Given Mass of Solute
In [link], we found the typical concentration of vinegar to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?
Solution
First, use the molar mass to calculate moles of acetic acid from the given mass:
Equation:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:
Equation:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:
Equation:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Equation:

$$75.6 \text{ g } CH_3CO_2H \left(\frac{\text{mol } CH_3CO_2H}{60.05 \text{ g}} \right) \left(\frac{\text{L solution}}{0.839 \text{ mol } CH_3CO_2H} \right) = 1.50 \text{ L solution}$$

Check Your Learning

What volume of a 1.50-*M* KBr solution contains 66.0 g KBr?

Note:
Answer:
0.370 L

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste ([link]).
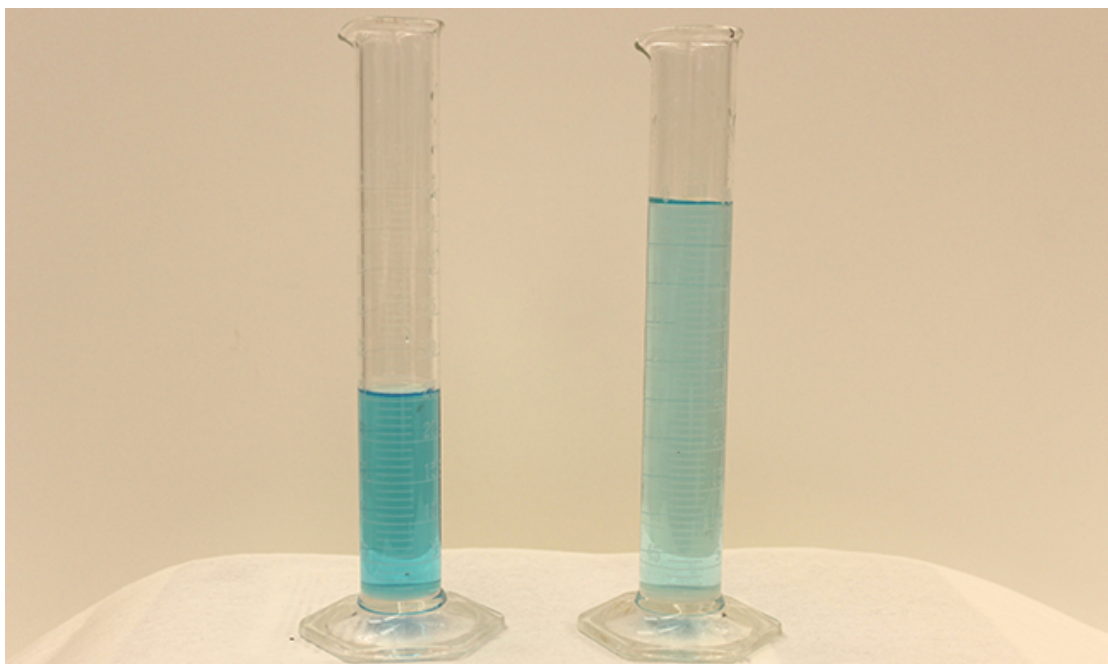
Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, we can achieve a particular concentration. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents ([link]).
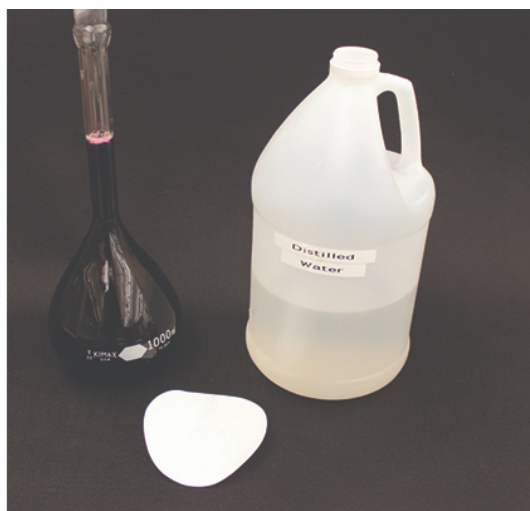
A solution of KMnO4 is prepared by mixing water with 4.74 g of KMnO4 in a flask. (credit: modification of work by Mark Ott)

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the molar amount of solute in a solution is equal to the product of the solution's molarity and its volume in liters:
Equation:

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:
Equation:

$$n_1 = M_1 L_1$$

Equation:

$$n_2 = M_2 L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution,* $n_1 = n_2$. Thus, these two equations may be set equal to one another:
Equation:

$$M_1 L_1 = M_2 L_2$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used, so long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

Equation:

$$C_1 V_1 = C_2 V_2$$

where C and V are concentration and volume, respectively.

Note:

Use the simulation to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

Example:

Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-M solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

Equation:

$$C_1 V_1 = C_2 V_2$$

$$C_2 = \frac{C_1 V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution's concentration to be less

than one-half 5 M. We will compare this ballpark estimate to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

Equation:

$$C_2 = \frac{0.850 \text{ L} \times 5.00 \frac{\text{mol}}{\text{L}}}{1.80 \text{ L}} = 2.36 \ M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 M).

Check Your Learning

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH_3OH to 500.0 mL?

Note:
Answer:
0.102 M CH_3OH

Example:
Volume of a Diluted Solution

What volume of 0.12 M HBr can be prepared from 11 mL (0.011 L) of 0.45 M HBr?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

Equation:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 M) is slightly more than one-fourth the original concentration (0.45 M), we would expect the volume of the diluted solution to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

Equation:

$$V_2 = \frac{(0.45\ M)(0.011\ \text{L})}{(0.12\ M)}$$

$$V_2 = 0.041\ \text{L}$$

The volume of the 0.12-M solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

Check Your Learning

A laboratory experiment calls for 0.125 M HNO_3. What volume of 0.125 M HNO_3 can be prepared from 0.250 L of 1.88 M HNO_3?

Note:
Answer:
3.76 L

Example:
Volume of a Concentrated Solution Needed for Dilution
What volume of 1.59 M KOH is required to prepare 5.00 L of 0.100 M KOH?
Solution
We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:
Equation:

$$C_1 V_1 = C_2 V_2$$

$$V_1 = \frac{C_2 V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 M is roughly one-sixteenth that of the stock solution (1.59 M), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:
Equation:

$$V_1 = \frac{(0.100\ M)(5.00\ \text{L})}{1.59\ M}$$
$$V_1 = 0.314\ \text{L}$$

Thus, we would need 0.314 L of the 1.59-*M* solution to prepare the desired solution. This result is consistent with our rough estimate.
Check Your Learning
What volume of a 0.575-*M* solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

Note:
Answer:
0.261 L

Key Concepts and Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

Chemistry End of Chapter Exercises

Exercise:

  Problem:

  Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

Exercise:

Problem:

What information do we need to calculate the molarity of a sulfuric acid solution?

Solution:

We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

Exercise:

Problem:

What does it mean when we say that a 200-mL sample and a 400-mL sample of a solution of salt have the same molarity? In what ways are the two samples identical? In what ways are these two samples different?

Exercise:

Problem: Determine the molarity for each of the following solutions:

(a) 0.444 mol of $CoCl_2$ in 0.654 L of solution

(b) 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution

(c) 0.2074 g of calcium hydroxide, $Ca(OH)_2$, in 40.00 mL of solution

(d) 10.5 kg of $Na_2SO_4 \cdot 10H_2O$ in 18.60 L of solution

(e) 7.0×10^{-3} mol of I_2 in 100.0 mL of solution

(f) 1.8×10^4 mg of HCl in 0.075 L of solution

Solution:

(a) 0.679 M;
(b) 1.00 M;
(c) 0.06998 M;
(d) 1.75 M;
(e) 0.070 M;
(f) 6.6 M

Exercise:

Problem: Determine the molarity of each of the following solutions:

(a) 1.457 mol KCl in 1.500 L of solution

(b) 0.515 g of H_2SO_4 in 1.00 L of solution

(c) 20.54 g of $Al(NO_3)_3$ in 1575 mL of solution

(d) 2.76 kg of $CuSO_4 \cdot 5H_2O$ in 1.45 L of solution

(e) 0.005653 mol of Br_2 in 10.00 mL of solution

(f) 0.000889 g of glycine, $C_2H_5NO_2$, in 1.05 mL of solution

Exercise:

Problem:

Consider this question: What is the mass of the solute in 0.500 L of 0.30 M glucose, $C_6H_{12}O_6$, used for intravenous injection?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass; (b) 27 g

Exercise:

Problem:

Consider this question: What is the mass of solute in 200.0 L of a 1.556-M solution of KBr?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:

Problem:

Calculate the number of moles and the mass of the solute in each of the following solutions:

(a) 2.00 L of 18.5 M H_2SO_4, concentrated sulfuric acid

(b) 100.0 mL of $3.8 \times 10^{-5}\ M$ NaCN, the minimum lethal concentration of sodium cyanide in blood serum

(c) 5.50 L of 13.3 M H_2CO, the formaldehyde used to "fix" tissue samples

(d) 325 mL of $1.8 \times 10^{-6}\ M$ $FeSO_4$, the minimum concentration of iron sulfate detectable by taste in drinking water

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Solution:

(a) 37.0 mol H_2SO_4;
3.63×10^3 g H_2SO_4;
(b) 3.8×10^{-6} mol NaCN;
1.9×10^{-4} g NaCN;
(c) 73.2 mol H_2CO;
2.20 kg H_2CO;
(d) 5.9×10^{-7} mol $FeSO_4$;
8.9×10^{-5} g $FeSO_4$

Exercise:

Problem:

Calculate the number of moles and the mass of the solute in each of the following solutions:

(a) 325 mL of $8.23 \times 10^{-5}\ M$ KI, a source of iodine in the diet

(b) 75.0 mL of $2.2 \times 10^{-5}\ M$ H_2SO_4, a sample of acid rain

(c) 0.2500 L of 0.1135 M K_2CrO_4, an analytical reagent used in iron assays

(d) 10.5 L of 3.716 M $(NH_4)_2SO_4$, a liquid fertilizer

Exercise:

Problem:

Consider this question: What is the molarity of $KMnO_4$ in a solution of 0.0908 g of $KMnO_4$ in 0.500 L of solution?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Solution:

(a) Determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity; (b) $1.15 \times 10^{-3}\ M$

Exercise:

Problem:

Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

Exercise:

Problem: Calculate the molarity of each of the following solutions:

(a) 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum

(b) 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia

(c) 1.49 kg of isopropyl alcohol, C_3H_7OH, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol

(d) 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20 °C

Solution:

(a) $5.04 \times 10^{-3}\ M$;
(b) $0.499\ M$;
(c) $9.92\ M$;
(d) $1.1 \times 10^{-3}\ M$

Exercise:

Problem: Calculate the molarity of each of the following solutions:

(a) 293 g HCl in 666 mL of solution, a concentrated HCl solution

(b) 2.026 g $FeCl_3$ in 0.1250 L of a solution used as an unknown in general chemistry laboratories

(c) 0.001 mg Cd^{2+} in 0.100 L, the maximum permissible concentration of cadmium in drinking water

(d) 0.0079 g $C_7H_5SNO_3$ in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.

Exercise:

Problem:

There is about 1.0 g of calcium, as Ca^{2+}, in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?

Solution:

0.025 M

Exercise:

Problem:

What volume of a 1.00-M $Fe(NO_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 M?

Exercise:

Problem:

If 0.1718 L of a 0.3556-M C_3H_7OH solution is diluted to a concentration of 0.1222 M, what is the volume of the resulting solution?

Solution:

0.5000 L

Exercise:

Problem:

If 4.12 L of a 0.850 M-H_3PO_4 solution is be diluted to a volume of 10.00 L, what is the concentration of the resulting solution?

Exercise:

Problem:

What volume of a 0.33-M $C_{12}H_{22}O_{11}$ solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 M?

Solution:

1.9 mL

Exercise:

Problem:

What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-M solution is allowed to evaporate until the volume is reduced to 0.105 L?

Exercise:

Problem:

What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?

(a) 1.00 L of a 0.250-M solution of $Fe(NO_3)_3$ is diluted to a final volume of 2.00 L

(b) 0.5000 L of a 0.1222-M solution of C_3H_7OH is diluted to a final volume of 1.250 L

(c) 2.35 L of a 0.350-M solution of H_3PO_4 is diluted to a final volume of 4.00 L

(d) 22.50 mL of a 0.025-M solution of $C_{12}H_{22}O_{11}$ is diluted to 100.0 mL

Solution:

(a) 0.125 M;
(b) 0.04888 M;
(c) 0.206 M;
(e) 0.0056 M

Exercise:

Problem:

What is the final concentration of the solution produced when 225.5 mL of a 0.09988-M solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

Exercise:

Problem:

A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution?

Solution:

11.9 M

Exercise:

Problem:

An experiment in a general chemistry laboratory calls for a 2.00-M solution of HCl. How many mL of 11.9 M HCl would be required to make 250 mL of 2.00 M HCl?

Key Equations

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Glossary

aqueous solution
    solution for which water is the solvent

concentrated
    qualitative term for a solution containing solute at a relatively high concentration

concentration
    quantitative measure of the relative amounts of solute and solvent present in a solution

dilute
    qualitative term for a solution containing solute at a relatively low concentration

dilution
    process of adding solvent to a solution in order to lower the concentration of solutes

dissolved
    describes the process by which solute components are dispersed in a solvent

molarity (M)
    unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute
    solution component present in a concentration less than that of the solvent

solvent

solution component present in a concentration that is higher relative to other components

Other Units for Solution Concentrations
By the end of this section, you will be able to:

- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- Perform computations relating a solution's concentration and its components' volumes and/or masses using these units

In the previous section, we introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. In this section, we will introduce some other units of concentration that are commonly used in various applications, either for convenience or by convention.

Mass Percentage

Earlier in this chapter, we introduced percent composition as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The **mass percentage** of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

Equation:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\%$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent.

Mass percentage is also referred to by similar names such as *percent mass, percent weight, weight/weight percent,* and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle ([link]) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.

Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.

Example:
Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

Equation:

$$\% \text{ glucose} = \frac{3.75 \text{ mg glucose} \times \frac{1\,\text{g}}{1000\,\text{mg}}}{5.0 \text{ g spinal fluid}} = 0.075\,\%$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, we converted the units of solute in the numerator from mg to g to match the units in the denominator. We could just as easily have converted the denominator from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

Check Your Learning

A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?

Note:

Answer:

14.8%

Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a **volume percentage**, %vol or (v/v)%:

Equation:

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

Mass-Volume Percentage

"Mixed" percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A **mass-volume percent** is a ratio of a solute's mass to the solution's volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as "blood sugar") is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood ([link]).

"Mixed" mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by "The National Guard"/Flickr; credit b: modification of work by Biswarup Ganguly)

Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as **parts per million (ppm)** or **parts per billion (ppb)**. Like percentage ("part per hundred") units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:
Equation:

$$\mathrm{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \, \mathrm{ppm}$$

$$\mathrm{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \, \mathrm{ppb}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water ([link]).

(a) (b)

(a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons)

Example:

Calculation of Parts per Million and Parts per Billion Concentrations
According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution
The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

Equation:

$$15 \, \text{ppb} \; \times \; \frac{1 \, \text{ppm}}{10^3 \, \text{ppb}} = 0.015 \, \text{ppm}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

Equation:

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \, \text{ppb}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \, \text{ppb}}$$

$$\text{mass solute} = \frac{15 \, \text{ppb} \times 300 \, \text{mL} \times \frac{1.00 \, \text{g}}{\text{mL}}}{10^9 \, \text{ppb}} = 4.5 \; \times \; 10^{-6} \, \text{g}$$

Finally, convert this mass to the requested unit of micrograms:

Equation:

$$4.5 \times 10^{-6}\,\text{g} \times \frac{1\,\mu\text{g}}{10^{-6}\,\text{g}} = 4.5\,\mu\text{g}$$

Check Your Learning

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Note:

Answer:

9.6 ppm, 9600 ppb

Section Summary

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

Exercise:

  Problem:

  What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?

Exercise:

Problem:

The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $CaCO_3$, which is equivalent to milligrams of $CaCO_3$ per liter of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?

Solution:

$1.75 \times 10^{-3}\ M$

Exercise:

Problem:

Copper(I) iodide (CuI) is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?

Solution:

$2.38 \times 10^{-4}\ \text{mol}$

Exercise:

Problem:

D5W is a solution used as an intravenous fluid. It is a 5.0% by mass solution of dextrose ($C_6H_{12}O_6$) in water. If the density of D5W is 1.029 g/mL, calculate the molarity of dextrose in the solution.

Solution:

0.29 mol

Exercise:

Problem:

Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid, H_2SO_4, for which the density is 1.3057 g/mL.

Key Equations

- Percent by mass $= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$
- ppm $= \frac{\text{mass solute}}{\text{mass solution}} \times 10^6$ ppm
- ppb $= \frac{\text{mass solute}}{\text{mass solution}} \times 10^9$ ppb

Glossary

mass percentage
    ratio of solute-to-solution mass expressed as a percentage

mass-volume percent
    ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)
    ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm)
    ratio of solute-to-solution mass multiplied by 10^6

volume percentage
    ratio of solute-to-solution volume expressed as a percentage

Introduction

- Writing and Balancing Chemical Equations
- Classifying Chemical Reactions
- Reaction Stoichiometry
- Reaction Yields
- Quantitative Chemical Analysis

Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. (credit: modification of work by NASA)

Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet ([link]). The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

Writing and Balancing Chemical Equations
By the end of this section, you will be able to:

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

The preceding chapter introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of [link], with space-filling molecular models shown in the lower half of the figure.
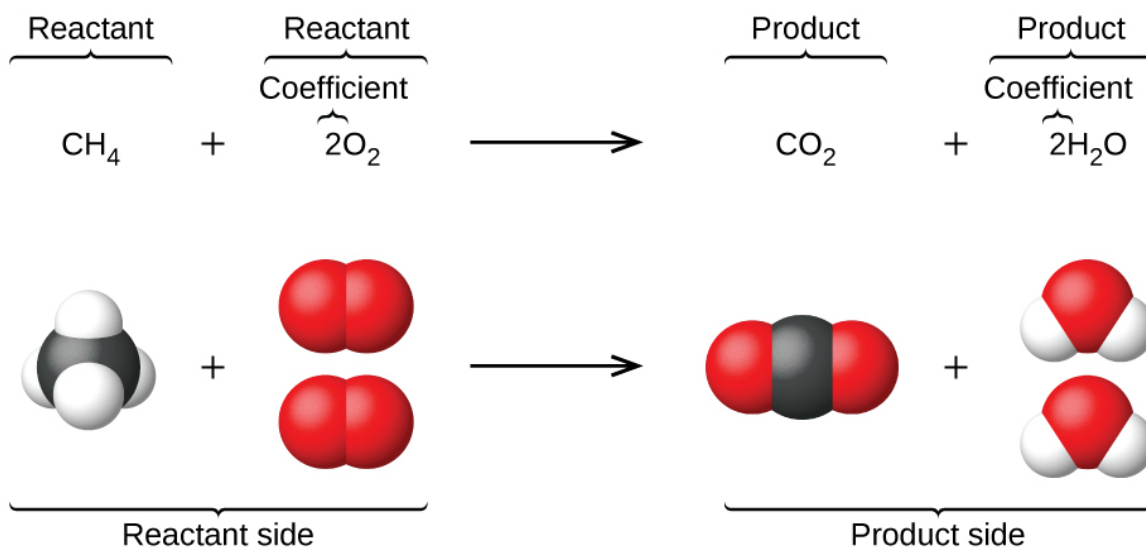
The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called **products**, and their formulas are placed on the right sight of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow ($\longrightarrow$) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on ([link]). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.
- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

Mixture before reaction   Mixture after reaction
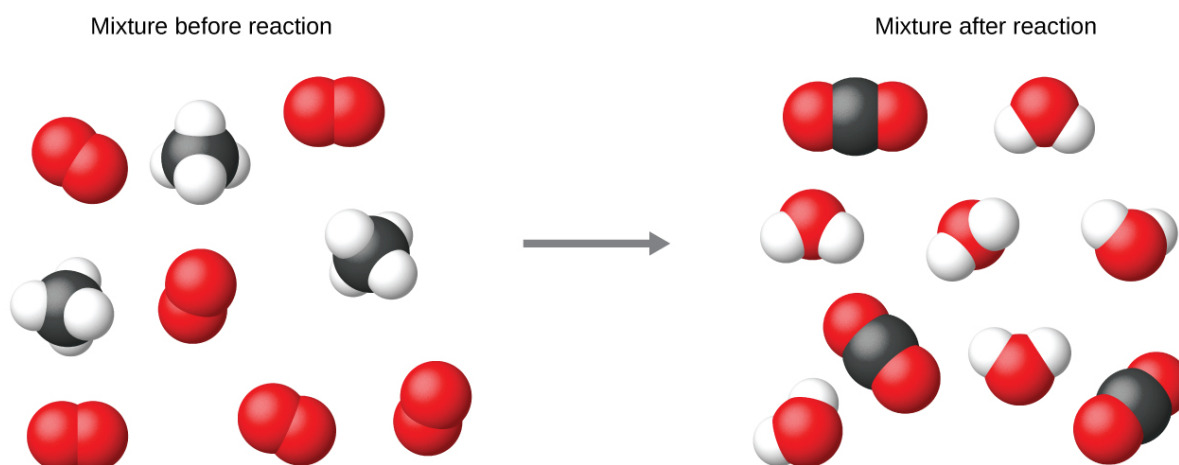
Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

Balancing Equations

The chemical equation described in section 4.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is
Equation:

$$\left(1\,CO_2\,\text{molecule}\ \times\ \frac{2\,\text{O atoms}}{CO_2\,\text{molecule}}\right)\ +\ \left(2\,H_2O\,\text{molecule}\ \times\ \frac{1\,\text{O atom}}{H_2O\,\text{molecule}}\right)\ =\ 4\,\text{O atoms}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:
Equation:

$$CH_4 + 2O_2 \ \longrightarrow\ CO_2 + 2H_2O$$
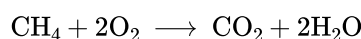
Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:
Equation:

$$H_2O \longrightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$
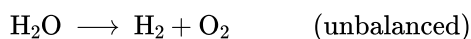
Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.
Equation:

$$\mathbf{2}H_2O \longrightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$
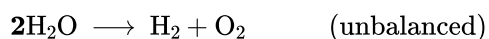
Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.
Equation:

$$2H_2O \longrightarrow \textbf{2}H_2 + O_2 \qquad \text{(balanced)}$$
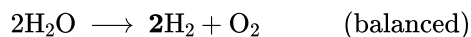
Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$\textbf{2} \times 2 = 4$	4 = 4, yes
O	$2 \times 1 = 2$	$1 \times 2 = 2$	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:
Equation:

$$2H_2O \longrightarrow 2H_2 + O_2$$
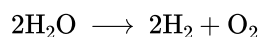
Example:
Balancing Chemical Equations
Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.
Solution
First, write the unbalanced equation.
Equation:

$$N_2 + O_2 \longrightarrow N_2O_5 \qquad \text{(unbalanced)}$$
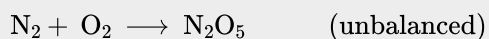
Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$1 \times 2 = 2$	2 = 2, yes
O	$1 \times 2 = 2$	$1 \times 5 = 5$	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).
Equation:

$$N_2 + \textbf{5}O_2 \longrightarrow \textbf{2}N_2O_5 \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.
Equation:

$$2N_2 + 5O_2 \longrightarrow 2N_2O_5$$
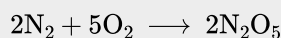
Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.
Check Your Learning
Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Note:
Answer:
$$2NH_4NO_3 \longrightarrow 2N_2 + O_2 + 4H_2O$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,
Equation:

$$3N_2 + 9H_2 \longrightarrow 6NH_3$$
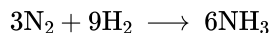
the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:
Equation:
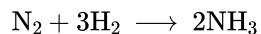
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

Equation:

$$2\text{Na}(\ ) + 2\text{H}_2\text{O}(\ ) \longrightarrow 2\text{NaOH}(\ ) + \text{H}_2(\ )$$
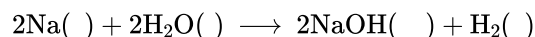
This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

Equation:

$$\text{CaCO}_3(\ ) \xrightarrow{\Delta} \text{CaO}(\ ) + \text{CO}_2(\ )$$
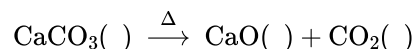
Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of CaCl_2 and AgNO_3 are mixed, a reaction takes place producing aqueous $\text{Ca(NO}_3)_2$ and solid AgCl:

Equation:

$$\text{CaCl}_2(\ ) + 2\text{AgNO}_3(\ ) \longrightarrow \text{Ca(NO}_3)_2(\ ) + 2\text{AgCl}(\ )$$
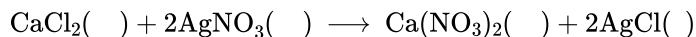
This balanced equation, derived in the usual fashion, is called a **molecular equation** because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

Equation:

$$CaCl_2(\quad) \longrightarrow Ca^{2+}(\quad) + 2Cl^-(\quad)$$
$$2AgNO_3(\quad) \longrightarrow 2Ag^+(\quad) + 2NO_3^-(\quad)$$
$$Ca(NO_3)_2(\quad) \longrightarrow Ca^{2+}(\quad) + 2NO_3^-(\quad)$$
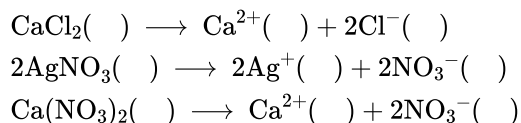
Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *s*.

Explicitly representing all dissolved ions results in a **complete ionic equation**. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:
Equation:

$$Ca^{2+}(\quad) + 2Cl^-(\quad) + 2Ag^+(\quad) + 2NO_3^-(\quad) \longrightarrow Ca^{2+}(\quad) + 2NO_3^-(\quad) + 2AgCl(\quad)$$
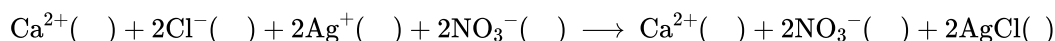
Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $Ca^{2+}(aq)$ and $NO_3^-(\quad)$. These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:
Equation:

$$\cancel{Ca^{2+}(\quad)} + 2Cl^-(\quad) + 2Ag^+(\quad) + \cancel{2NO_3^-(\quad)} \longrightarrow \cancel{Ca^{2+}(\quad)} + \cancel{2NO_3^-(\quad)} + 2AgCl(\quad)$$
$$2Cl^-(\quad) + 2Ag^+(\quad) \longrightarrow 2AgCl(\quad)$$
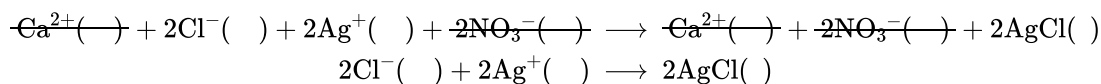
Following the convention of using the smallest possible integers as coefficients, this equation is then written:
Equation:

$$Cl^-(\quad) + Ag^+(\quad) \longrightarrow AgCl(\quad)$$
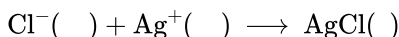
This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+.

Example:
Molecular and Ionic Equations
When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.
Solution
Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:
Equation:

$$CO_2(\quad) + NaOH(\quad) \longrightarrow Na_2CO_3(\quad) + H_2O(\quad) \qquad \text{(unbalanced)}$$
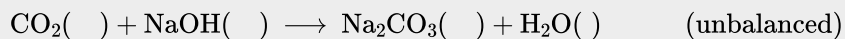
Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:
Equation:

$$CO_2(\quad) + 2NaOH(\quad) \longrightarrow Na_2CO_3(\quad) + H_2O(\quad)$$
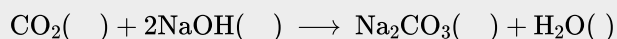
The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as dissociated ions to yield the complete ionic equation:
Equation:

$$CO_2(\ ) + 2Na^+(\ ) + 2OH^-(\ ) \longrightarrow 2Na^+(\ ) + CO_3{}^{2-}(\ ) + H_2O(\ )$$
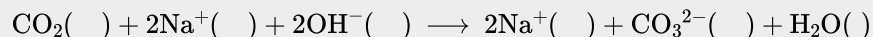
Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:
Equation:

$$CO_2(\ ) + \cancel{2Na^+(\ )} + 2OH^-(\ ) \longrightarrow \cancel{2Na^+(\ )} + CO_3{}^{2-}(\ ) + H_2O(\ )$$
$$CO_2(\ ) + 2OH^-(\ ) \longrightarrow CO_3{}^{2-}(\ ) + H_2O(\ )$$
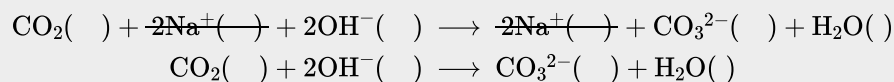
Check Your Learning
Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:
Equation:

$$NaCl(\ ) + H_2O(\ ) \xrightarrow{\text{electricity}} NaOH(\ ) + H_2(\ ) + Cl_2(\ )$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Note:
Answer:
$2NaCl(\ ) + 2H_2O(\ ) \longrightarrow 2NaOH(\ ) + H_2(\ ) + Cl_2(\ ) \qquad$ (molecular)
$2Na^+(\ ) + 2Cl^-(\ ) + 2H_2O(\ ) \longrightarrow 2Na^+(\ ) + 2OH^-(\ ) + H_2(\ ) + Cl_2(\ ) \qquad$ (complete ionic)
$2Cl^-(\ ) + 2H_2O(\ ) \longrightarrow 2OH^-(\ ) + H_2(\ ) + Cl_2(\ ) \qquad$ (net ionic)
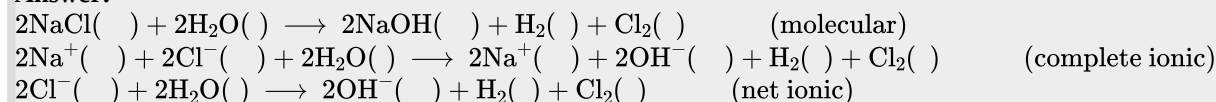
Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Chemistry End of Chapter Exercises

Exercise:

Problem:

What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

Solution:

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

Exercise:

Problem: Consider molecular, complete ionic, and net ionic equations.

(a) What is the difference between these types of equations?

(b) In what circumstance would the complete and net ionic equations for a reaction be identical?

Exercise:

Problem: Balance the following equations:

(a) $PCl_5(\ ) + H_2O(\ ) \longrightarrow POCl_3(\ ) + HCl(\ )$

(b) $Cu(\ ) + HNO_3(\ ) \longrightarrow Cu(NO_3)_2(\ ) + H_2O(\ ) + NO(\ )$

(c) $H_2(\ ) + I_2(\ ) \longrightarrow HI(\ )$

(d) $Fe(\ ) + O_2(\ ) \longrightarrow Fe_2O_3(\ )$

(e) $Na(\ ) + H_2O(\ ) \longrightarrow NaOH(\ ) + H_2(\ )$

(f) $(NH_4)_2Cr_2O_7(\ ) \longrightarrow Cr_2O_3(\ ) + N_2(\ ) + H_2O(\ )$

(g) $P_4(\ ) + Cl_2(\ ) \longrightarrow PCl_3(\ )$

(h) $PtCl_4(\ ) \longrightarrow Pt(\ ) + Cl_2(\ )$
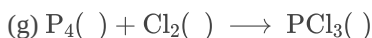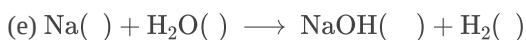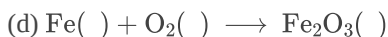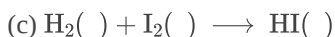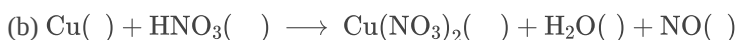
Solution:

(a) $PCl_5(\ ) + H_2O(\ ) \longrightarrow POCl_3(\ ) + 2HCl(\ )$; (b) $3Cu(\ ) + 8HNO_3(\ ) \longrightarrow 3Cu(NO_3)_2(\ ) + 4H_2O(\ ) + 2NO(\ )$; (c) $H_2(\ ) + I_2(\ ) \longrightarrow 2HI(\ )$; (d) $4Fe(\ ) + 3O_2(\ ) \longrightarrow 2Fe_2O_3(\ )$; (e) $2Na(\ ) + 2H_2O(\ ) \longrightarrow 2NaOH(\ ) + H_2(\ )$; (f) $(NH_4)_2Cr_52O_7(\ ) \longrightarrow Cr_2O_3(\ ) + N_2(\ ) + 4H_2O(\ )$; (g) $P_4(\ ) + 6Cl_2(\ ) \longrightarrow 4PCl_3(\ )$; (h) $PtCl_4(\ ) \longrightarrow Pt(\ ) + 2Cl_2(\ )$

Exercise:

Problem: Balance the following equations:

(a) $Ag(\ ) + H_2S(\ ) + O_2(\ ) \longrightarrow Ag_2S(\ ) + H_2O(\ )$

(b) $P_4(\ ) + O_2(\ ) \longrightarrow P_4O_{10}(\ )$

(c) $Pb(\ ) + H_2O(\ ) + O_2(\ ) \longrightarrow Pb(OH)_2(\ )$

(d) $Fe(\ ) + H_2O(\ ) \longrightarrow Fe_3O_4(\ ) + H_2(\ )$

(e) $Sc_2O_3(\ ) + SO_3(\ ) \longrightarrow Sc_2(SO_4)_3(\ )$

(f) $Ca_3(PO_4)_2(\ ) + H_3PO_4(\ ) \longrightarrow Ca(H_2PO_4)_2(\ )$

(g) $Al(\ ) + H_2SO_4(\ ) \longrightarrow Al_2(SO_4)_3(\ ) + H_2(\ )$

(h) $TiCl_4(\ ) + H_2O(\ ) \longrightarrow TiO_2(\ ) + HCl(\ )$
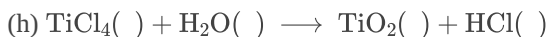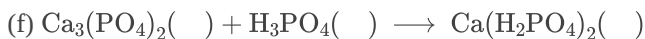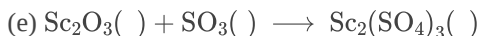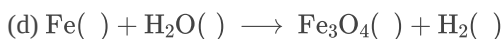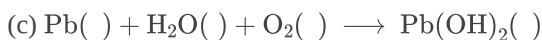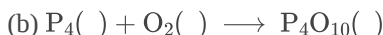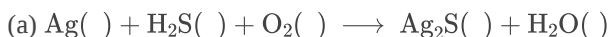
Exercise:

Problem: Write a balanced molecular equation describing each of the following chemical reactions.

(a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.

(b) Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.

(c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.

(d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

Solution:

(a) $CaCO_3(\ ) \longrightarrow CaO(\ ) + CO_2(\ )$; (b) $2C_4H_{10}(\ ) + 13O_2(\ ) \longrightarrow 8CO_2(\ ) + 10H_2O(\ )$; (c) $MgC1_2(\ ) + 2NaOH(\ ) \longrightarrow Mg(OH)_2(\ ) + 2NaCl(\ )$; (d) $2H_2O(\ ) + 2Na(\ ) \longrightarrow 2NaOH(\ ) + H_2(\ )$

Exercise:

Problem: Write a balanced equation describing each of the following chemical reactions.

(a) Solid potassium chlorate, $KClO_3$, decomposes to form solid potassium chloride and diatomic oxygen gas.

(b) Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6.

(c) When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.

(d) Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

Exercise:

Problem:

Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

(a) Write the formulas of barium nitrate and potassium chlorate.

(b) The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.

(c) The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.

(d) Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

Solution:

(a) $Ba(NO_3)_2$, $KClO_3$; (b) $2KClO_3(\ ) \longrightarrow 2KCl(\ ) + 3O_2(\ )$; (c) $2Ba(NO_3)_2(\ ) \longrightarrow 2BaO(\ ) + 2N_2(\ ) + 5O_2(\ )$; (d) $2Mg(\ ) + O_2(\ ) \longrightarrow 2MgO(\ )$; $4Al(\ ) + 3O_2(\ ) \longrightarrow 2Al_2O_3(\ )$; $4Fe(\ ) + 3O_2(\ ) \longrightarrow 2Fe_2O_3(\ )$

Exercise:

Problem:

Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:

$$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ | \quad\ \ | \quad\ \ || \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\ | \quad\ \ | \\ \text{H} \quad \text{H} \end{array} \ + \ \text{NaOH} \ \longrightarrow \ \begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\ | \quad\ \ | \quad\ \ || \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}^- \\ | \quad\ \ | \\ \text{H} \quad \text{H} \end{array} \ + \ \text{Na}^+ \ + \ \underline{\quad\quad}$$
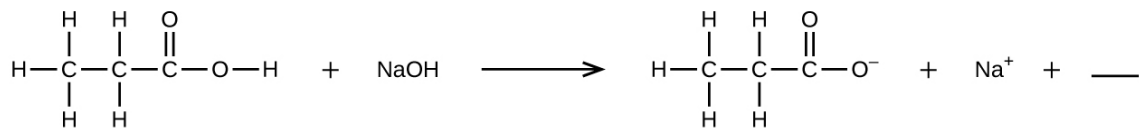
Exercise:

Problem:

Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

(a) Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.

(b) The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

Solution:

(a) $4\text{HF}(\ \ ) + \text{SiO}_2(\ \ ) \longrightarrow \text{SiF}_4(\ \ ) + 2\text{H}_2\text{O}(\ \ )$; (b) complete ionic equation: $2\text{Na}^+(\ \ ) + 2\text{F}^-(\ \ ) + \text{Ca}^{2+}(\ \ ) + 2\text{Cl}^-(\ \ ) \longrightarrow \text{CaF}_2(\ \ ) + 2\text{Na}^+(\ \ ) + 2\text{Cl}^-(\ \ )$, net ionic equation: $2\text{F}^-(\ \ ) + \text{Ca}^{2+}(\ \ ) \longrightarrow \text{CaF}_2(\ \ )$

Exercise:

Problem:

A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

(a) The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.

(b) The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.

(c) Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.

(d) The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.

(e) Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

Exercise:

Problem:

From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

(a) $\text{K}_2\text{C}_2\text{O}_4(\ \ ) + \text{Ba(OH)}_2(\ \ ) \longrightarrow 2\text{KOH}(\ \ ) + \text{BaC}_2\text{O}_2(\ \ )$

(b) $Pb(NO_3)_2(\quad) + H_2SO_4(\quad) \longrightarrow PbSO_4(\quad) + 2HNO_3(\quad)$

(c) $CaCO_3(\quad) + H_2SO_4(\quad) \longrightarrow CaSO_4(\quad) + CO_2(\quad) + H_2O(\quad)$

Solution:

(a)

$2K^+(\quad) + C_2O_4{}^{2-}(\quad) + Ba^{2+}(\quad) + 2OH^-(\quad) \longrightarrow 2K^+(\quad) + 2OH^-(\quad) + BaC_2O_4(\quad)$ (comp

$Ba^{2+}(\quad) + C_2O_4{}^{2-}(\quad) \longrightarrow BaC_2O_4(\quad)$ (net)

(b)

$Pb^{2+}(\quad) + 2NO_3{}^-(\quad) + 2H^+(\quad) + SO_4{}^{2-}(\quad) \longrightarrow PbSO_4(\quad) + 2H^+(\quad) + 2NO_3{}^-(\quad)$ (comp

$Pb^{2+}(\quad) + SO_4{}^{2-}(\quad) \longrightarrow PbSO_4(\quad)$ (net)

(c)

$CaCO_3(\quad) + 2H^+(\quad) + SO_4{}^{2-}(\quad) \longrightarrow CaSO_4(\quad) + CO_2(\quad) + H_2O(\quad)$ (complete)

$CaCO_3(\quad) + 2H^+(\quad) + SO_4{}^{2-}(\quad) \longrightarrow CaSO_4(\quad) + CO_2(\quad) + H_2O(\quad)$ (net)
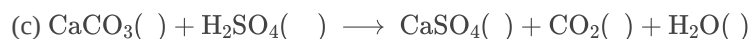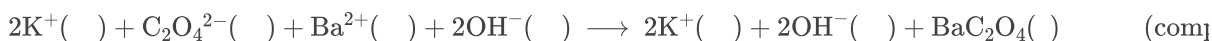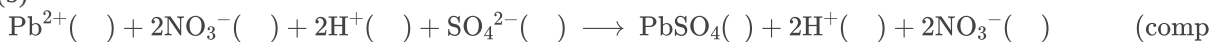
Glossary

balanced equation
 chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation
 symbolic representation of a chemical reaction

coefficient
 number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation
 chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation
 chemical equation in which all reactants and products are represented as neutral substances

net ionic equation
 chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product
 substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant
 substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion
 ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Classifying Chemical Reactions
By the end of this section, you will be able to:

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: precipitation, acid-base, and oxidation-reduction.

Precipitation Reactions and Solubility Rules

A **precipitation reaction** is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its **solubility**, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be **soluble**. A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be **insoluble**, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in the text chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds ([link]).

Solubilities of Common Ionic Compounds in Water	
Soluble compounds contain • group 1 metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium ion (NH_4^+) • the halide ions (Cl^-, Br^-, and I^-) • the acetate ($C_2H_3O_2^-$), bicarbonate (HCO_3^-), nitrate (NO_3^-), and chlorate (ClO_3^-) ions • the sulfate (SO_4^{2-}) ion	**Exceptions** to these solubility rules include • halides of Ag^+, Hg_2^{2+}, and Pb^{2+} • sulfates of Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+}, and Sr^{2+}
Insoluble compounds contain • carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), phosphate (PO_4^{3-}), and sulfide (S^{2-}) ions • hydroxide ion (OH^-)	**Exceptions** to these insolubility rules include • compounds of these anions with group 1 metal cations and ammonium ion • hydroxides of group 1 metal cations and Ba^{2+}

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

Equation:

$$2KI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$$
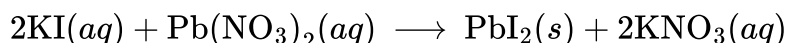
This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

Equation:

$$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$$
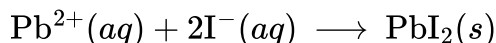
Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow ([link]). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.
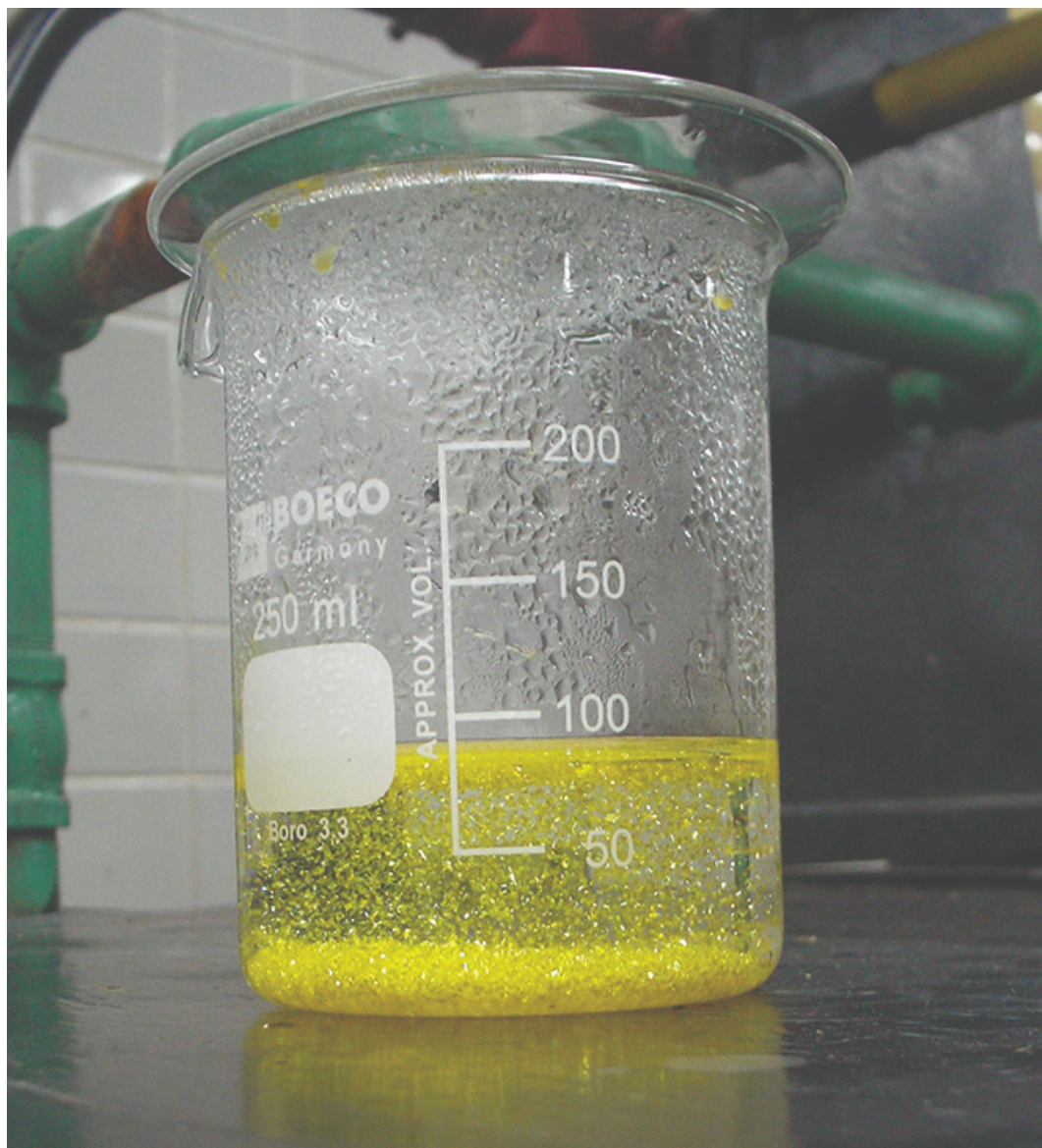
A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in [link] may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing Ag^+, NO_3^-, Na^+, and F^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaF, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgF. The solubility guidelines indicate all nitrate salts are soluble but that AgF is one of the exceptions

to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

Equation:

$$NaF(aq) + AgNO_3(aq) \longrightarrow AgF(s) + NaNO_3(aq) \qquad (molecular)$$

$$Ag^+(aq) + F^-(aq) \longrightarrow AgF(s) \qquad (net\ ionic)$$
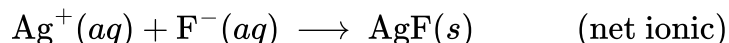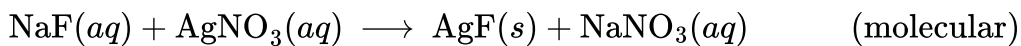
Example:
Predicting Precipitation Reactions
Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.
(a) potassium sulfate and barium nitrate
(b) lithium chloride and silver acetate
(c) lead nitrate and ammonium carbonate

Solution
(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

Equation:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$
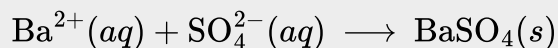
(b) The two possible products for this combination are $LiC_2H_3O_2$ and $AgCl$. The solubility guidelines indicate $AgCl$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

Equation:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$
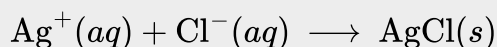
(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

Equation:

$$Pb^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow PbCO_3(s)$$
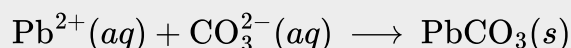
Check Your Learning
Which solution could be used to precipitate the barium ion, Ba^{2+}, in a water sample: sodium chloride, sodium hydroxide, or sodium sulfate? What is the formula for the expected precipitate?

Acid-Base Reactions

An **acid-base reaction** is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here:

Equation:

$$HCl(aq) + H_2O(aq) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$
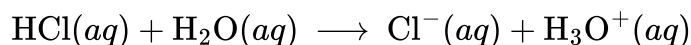
The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules ([link]).
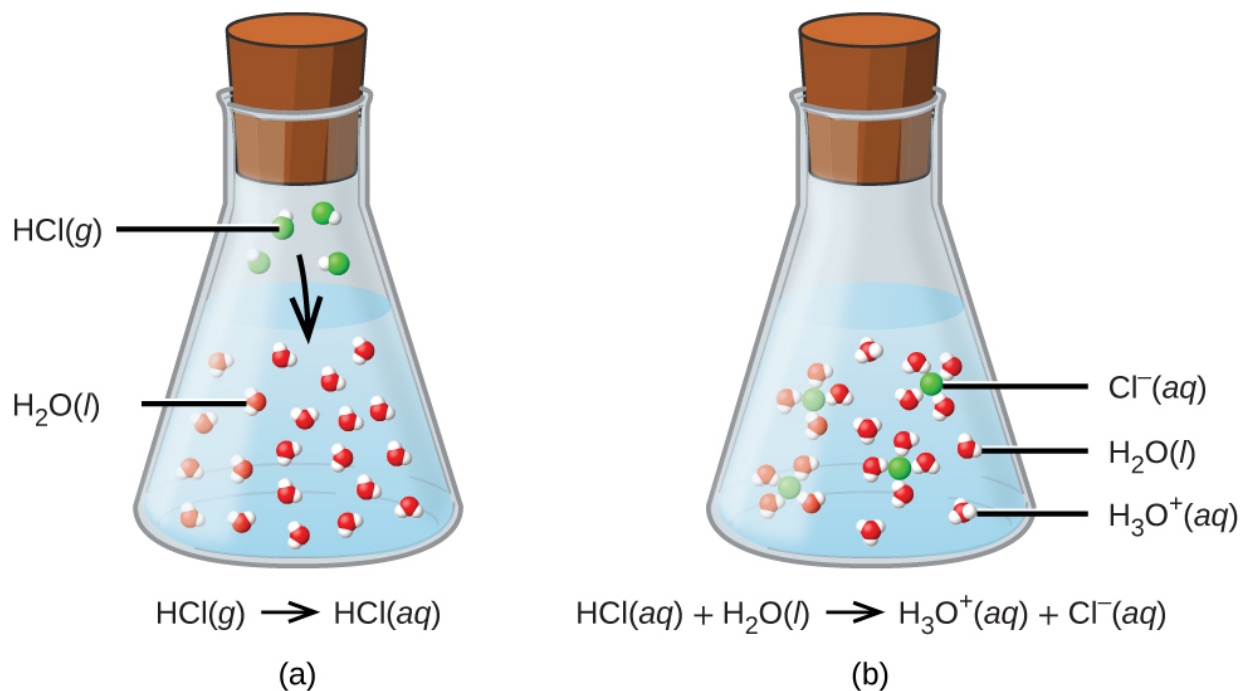
When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong ([link]). A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

Equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2{}^-(aq) + H_3O^+(aq)$$
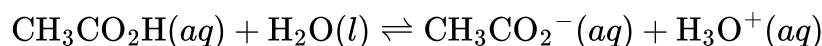
When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, $CH_3CO_2{}^-$ ([link]). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)
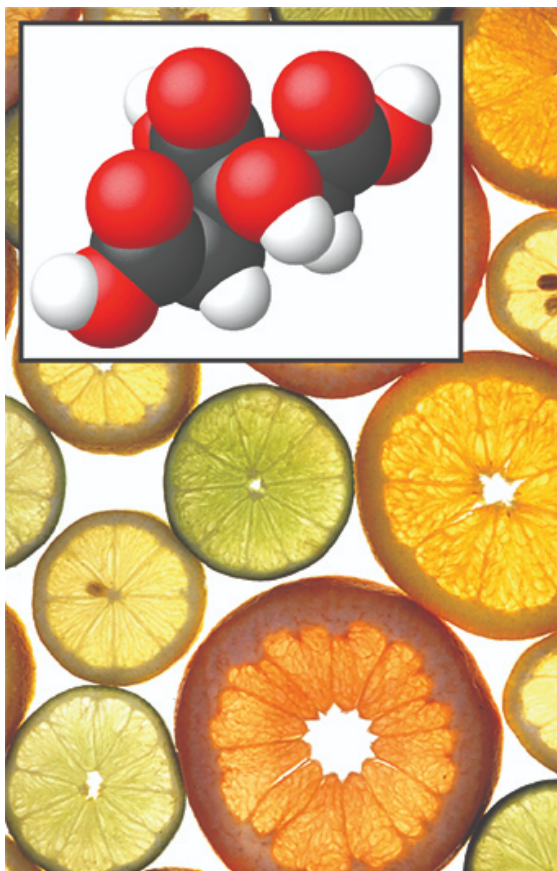
(a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

Common Strong Acids	
Compound Formula	**Name in Aqueous Solution**
HBr	hydrobromic acid
HCl	hydrochloric acid

Common Strong Acids	
Compound Formula	**Name in Aqueous Solution**
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

A **base** is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$. When these compounds dissolve in water, hydroxide ions are released directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in water, are considered **strong bases**.

Consider as an example the dissolution of lye (sodium hydroxide) in water:
Equation:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$
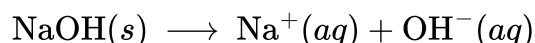
This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^+ and OH^- ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners ([link]). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:
Equation:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
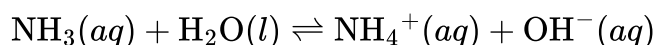
This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as NH_4^+ ions.

(a) (b)

Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

The chemical reactions described in which acids and bases dissolved in water produce hydronium and hydroxide ions, respectively, are, by definition, acid-base reactions. In these reactions, water serves as both a solvent *and* a reactant. A **neutralization reaction** is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often a **salt** and water, and neither reactant is the water itself:

Equation:

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$
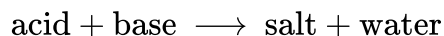
To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

Equation:

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l).$$
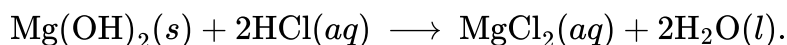
Note that in addition to water, this reaction produces a salt, magnesium chloride.

Example:

Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:

(a) the weak acid hydrogen hypochlorite reacts with water

(b) a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

Equation:

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$$
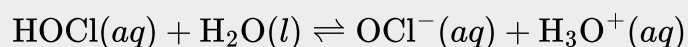
A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion $(NO_3{}^-)$.

Equation:

$$Ba(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$$

Check Your Learning

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Note:
Answer:
$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$
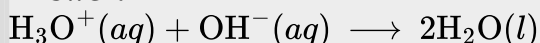
Note:

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:
Equation:

$$2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$$
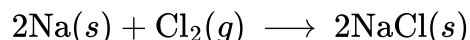
It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:
Equation:

$$2\text{Na}(s) \longrightarrow 2\text{Na}^+(s) + 2\text{e}^-$$
$$\text{Cl}_2(g) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(s)$$
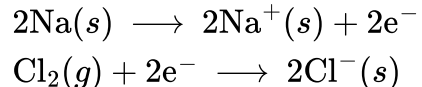
These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:
Equation:

$$= \text{ loss of electrons}$$
$$= \text{ gain of electrons}$$
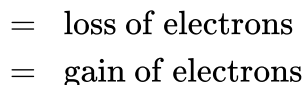
In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium.
Equation:

$$= \text{ species that is oxidized}$$
$$= \text{ species that is reduced}$$
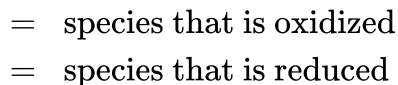
Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

Equation:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
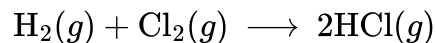
The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:

    o Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
    o Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, $O_2{}^{2-}$), very rarely $-\frac{1}{2}$ (so-called superoxides, $O_2{}^-$), positive values when combined with F (values vary)
    o Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)

4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example:
Assigning Oxidation Numbers
Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:
(a) H_2S
(b) $SO_3{}^{2-}$
(c) Na_2SO_4
Solution
(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

Equation:

$$\text{charge on } H_2S = 0 = (2 \times +1) + (1 \times x)$$
$$x = 0 - (2 \times +1) = -2$$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.
Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

Equation:

$$\text{charge on } SO_3{}^{2-} = -2 = (3 \times -2) + (1 \times x)$$
$$x = -2 - (3 \times -2) = +4$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.
According to guideline 2, the oxidation number for sodium is +1.
Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

Equation:

$$\text{charge on } SO_4{}^{2-} = -2 = (4 \times -2) + (1 \times x)$$
$$x = -2 - (4 \times -2) = +6$$

Check Your Learning
Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:
(a) K$\underline{N}$O$_3$
(b) $\underline{Al}$H$_3$
(c) $\underline{N}$H$_4{}^{+}$
(d) H$_2$$\underline{P}O_4{}^{-}$

Note:
Answer:
(a) N, +5; (b) Al, +3; (c) N, −3; (d) P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist [link].) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

Equation:

$$= \quad \text{increase in oxidation number}$$
$$= \quad \text{decrease in oxidation number}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions such as the one depicted in [link] are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

Equation:

$$10\text{Al}(s) + 6\text{NH}_4\text{ClO}_4(s) \longrightarrow 4\text{Al}_2\text{O}_3(s) + 2\text{AlCl}_3(s) + 12\text{H}_2\text{O}(g) + 3\text{N}_2(g)$$

Note:

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:
Equation:

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:
Equation:

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color ([link]).

(a)   (b)   (c)

(a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example:
Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

(a) $ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$

(b) $2Ga(l) + 3Br_2(l) \longrightarrow 2GaBr_3(s)$

(c) $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

(d) $BaCl_2(aq) + K_2SO_4(aq) \longrightarrow BaSO_4(s) + 2KCl(aq)$

(e) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

(a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(b) This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(l) to +3 in GaBr$_3$(s). The reducing agent is Ga(l). Bromine is reduced, its oxidation number decreasing from 0 in Br$_2$(l) to −1 in GaBr$_3$(s). The oxidizing agent is Br$_2$(l).

(c) This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction*). Oxygen is oxidized, its oxidation number increasing from −1 in H$_2$O$_2$(aq) to 0 in O$_2$(g). Oxygen is also reduced, its oxidation number decreasing from −1 in H$_2$O$_2$(aq) to −2 in H$_2$O(l). For disproportionation reactions, the same substance functions as an oxidant and a reductant.

(d) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C$_2$H$_4$(g) to +4 in CO$_2$(g). The reducing agent (fuel) is C$_2$H$_4$(g). Oxygen is reduced, its oxidation number decreasing from 0 in O$_2$(g) to −2 in H$_2$O(l). The oxidizing agent is O$_2$(g).

Check Your Learning

This equation describes the production of tin(II) chloride:

Equation:

$$Sn(s) + 2HCl(g) \longrightarrow SnCl_2(s) + H_2(g)$$
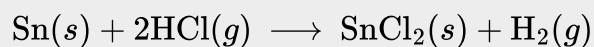
Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Note:

Answer:

Yes, a single-replacement reaction. Sn(s) is the reductant, HCl(g) is the oxidant.

Key Concepts and Summary

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and oxidation-reduction (redox). Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants. Redox reactions involve a change in oxidation number for one or more reactant elements.

Chemistry End of Chapter Exercises

Exercise:

Problem: Use the following equations to answer the next five questions:

i. $H_2O(s) \longrightarrow H_2O(l)$

ii.
$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3{}^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3{}^-(aq)$

iii. $CH_3OH(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

iv. $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

v. $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
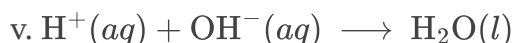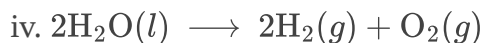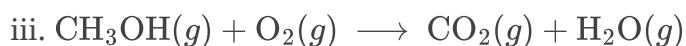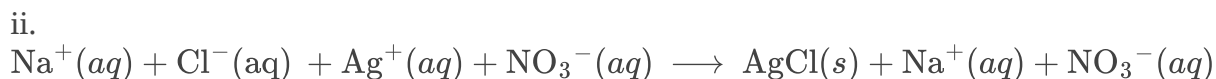
(a) Which equation describes a physical change?

(b) Which equation identifies the reactants and products of a combustion reaction?

(c) Which equation is not balanced?

(d) Which is a net ionic equation?

Exercise:

Problem: Indicate what type, or types, of reaction each of the following represents:

(a) $Ca(s) + Br_2(l) \longrightarrow CaBr_2(s)$

(b) $Ca(OH)_2(aq) + 2HBr(aq) \longrightarrow CaBr_2(aq) + 2H_2O(l)$

(c) $C_6H_{12}(l) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g)$
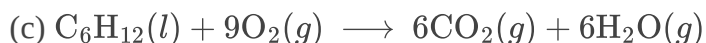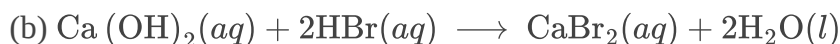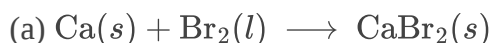
Solution:

(a) oxidation-reduction (addition); (b) acid-base (neutralization); (c) oxidation-reduction (combustion)

Exercise:

Problem: Indicate what type, or types, of reaction each of the following represents:

(a) $H_2O(g) + C(s) \longrightarrow CO(g) + H_2(g)$

(b) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$

(c) $Al(OH)_3(aq) + 3HCl(aq) \longrightarrow AlCl_3(aq) + 3H_2O(l)$

(d) $Pb(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2HNO_3(aq)$

Exercise:

Problem: Determine the oxidation states of the elements in the following compounds:

(a) NaI

(b) $GdCl_3$

(c) $LiNO_3$

(d) H_2Se

(e) Mg_2Si

(f) RbO_2, rubidium superoxide

(g) HF

Exercise:

Problem:

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a) H_3PO_4

(b) $Al(OH)_3$

(c) SeO_2

(d) KNO_2

(e) In_2S_3

(f) P_4O_6
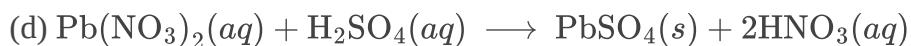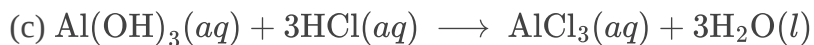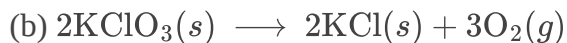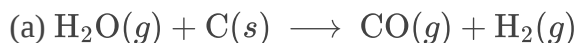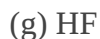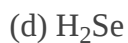
Solution:

(a) H +1, P +5, O −2; (b) Al +3, H +1, O −2; (c) Se +4, O −2; (d) K +1, N +3, O −2; (e) In +3, S −2; (f) P +3, O −2

Exercise:

Problem:

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a) H_2SO_4

(b) $Ca(OH)_2$

(c) BrOH

(d) $ClNO_2$

(e) $TiCl_4$

(f) NaH
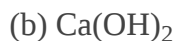
Exercise:

Problem: Classify the following as acid-base reactions or oxidation-reduction reactions:

(a) $Na_2S(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2S(g)$

(b) $2Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$

(c) $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

(d) $MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$

(e) $K_3P(s) + 2O_2(g) \longrightarrow K_3PO_4(s)$

(f) $3KOH(aq) + H_3PO_4(aq) \longrightarrow K_3PO_4(aq) + 3H_2O(l)$
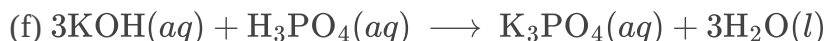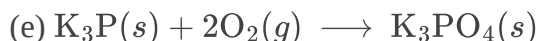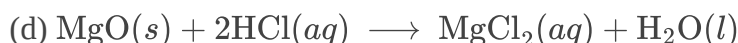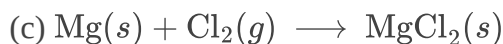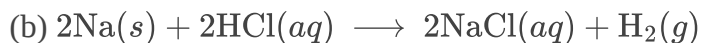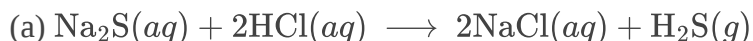
Solution:

(a) acid-base; (b) oxidation-reduction: Na is oxidized, H^+ is reduced; (c) oxidation-reduction: Mg is oxidized, Cl_2 is reduced; (d) acid-base; (e) oxidation-reduction: P^{3-} is oxidized, O_2 is reduced; (f) acid-base

Exercise:

Problem:

Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:
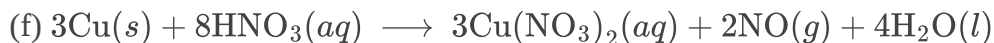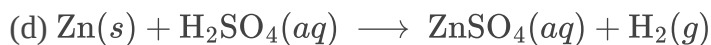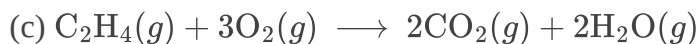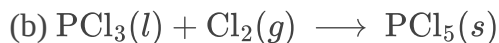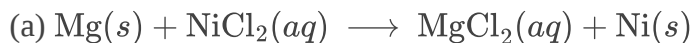
(a) $Mg(s) + NiCl_2(aq) \longrightarrow MgCl_2(aq) + Ni(s)$

(b) $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

(d) $Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$

(e) $2K_2S_2O_3(s) + I_2(s) \longrightarrow K_2S_4O_6(s) + 2KI(s)$

(f) $3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

Exercise:

Problem: Complete and balance the following acid-base equations:

(a) HCl gas reacts with solid $Ca(OH)_2(s)$.

(b) A solution of $Sr(OH)_2$ is added to a solution of HNO_3.

Solution:

(a) $2HCl(g) + Ca(OH)_2(s) \longrightarrow CaCl_2(s) + 2H_2O(l)$; (b)
$Sr(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Sr(NO_3)_2(aq) + 2H_2O(l)$

Exercise:

Problem: Complete and balance the following acid-base equations:

(a) A solution of $HClO_4$ is added to a solution of LiOH.

(b) Aqueous H_2SO_4 reacts with NaOH.

(c) $Ba(OH)_2$ reacts with HF gas.
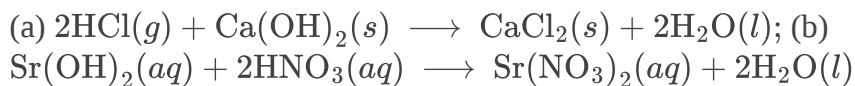
Exercise:

Problem:

The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?

Solution:

$H_2(g) + F_2(g) \longrightarrow 2HF(g)$
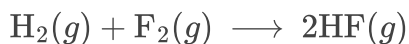
Exercise:

Problem:

Write the molecular, total ionic, and net ionic equations for the following reactions:

(a) $Ca(OH)_2(aq) + HC_2H_3O_2(aq) \longrightarrow$

(b) $H_3PO_4(aq) + CaCl_2(aq) \longrightarrow$
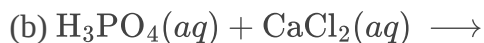
Exercise:

Problem:

Great Lakes Chemical Company produces bromine, Br_2, from bromide salts such as NaBr, in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of NaBr with Cl_2.

Solution:

$2NaBr(aq) + Cl_2(g) \longrightarrow 2NaCl(aq) + Br_2(l)$
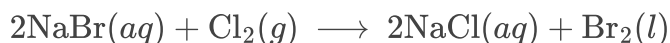
Exercise:

Problem:

Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO_2. (Hint: Water is one of the products.)

Solution:

$2LiOH(aq) + CO_2(g) \longrightarrow Li_2CO_3(aq) + H_2O(l)$
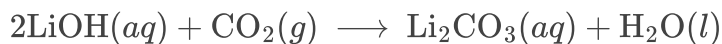
Exercise:

Problem:

Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, $CaCO_3$, with propionic acid, $C_2H_5CO_2H$, which has properties similar to those of acetic acid. Write the balanced equation for the formation of calcium propionate.

Glossary

acid
   substance that produces H_3O^+ when dissolved in water

acid-base reaction
   reaction involving the transfer of a hydrogen ion between reactant species

base
    substance that produces OH^- when dissolved in water

combustion reaction
    vigorous redox reaction producing significant amounts of energy in the form of heat
    and, sometimes, light

half-reaction
    an equation that shows whether each reactant loses or gains electrons in a reaction.

insoluble
    of relatively low solubility; dissolving only to a slight extent

neutralization reaction
    reaction between an acid and a base to produce salt and water

oxidation
    process in which an element's oxidation number is increased by loss of electrons

oxidation-reduction reaction
    (also, redox reaction) reaction involving a change in oxidation number for one or more
    reactant elements

oxidation number
    (also, oxidation state) the charge each atom of an element would have in a compound if
    the compound were ionic

oxidizing agent
    (also, oxidant) substance that brings about the oxidation of another substance, and in the
    process becomes reduced

precipitate
    insoluble product that forms from reaction of soluble reactants

precipitation reaction
    reaction that produces one or more insoluble products; when reactants are ionic
    compounds, sometimes called double-displacement or metathesis

reduction
    process in which an element's oxidation number is decreased by gain of electrons

reducing agent
    (also, reductant) substance that brings about the reduction of another substance, and in
    the process becomes oxidized

salt

ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide

single-displacement reaction
（also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

soluble
of relatively high solubility; dissolving to a relatively large extent

solubility
the extent to which a substance may be dissolved in water, or any solvent

strong acid
acid that reacts completely when dissolved in water to yield hydronium ions

strong base
base that reacts completely when dissolved in water to yield hydroxide ions

weak acid
acid that reacts only to a slight extent when dissolved in water to yield hydronium ions

weak base
base that reacts only to a slight extent when dissolved in water to yield hydroxide ions

Introduction

class="introduction"

- Energy Basics
- Calorimetry
- Enthalpy

Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes)

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[footnote] While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.

US Energy Information Administration, *Primary Energy Consumption by Source and Sector, 2012*, http://www.eia.gov/totalenergy/data/monthly/pdf/flow/css_2012_energy.pdf. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

Energy Basics
By the end of this section, you will be able to:

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world ([link]). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.
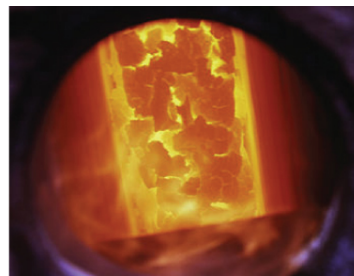
(a)   (b)   (c)

The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of **work (*w*)** is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move

matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant ([link]). A battery has potential energy because the chemicals within it can produce electricity that can do work.
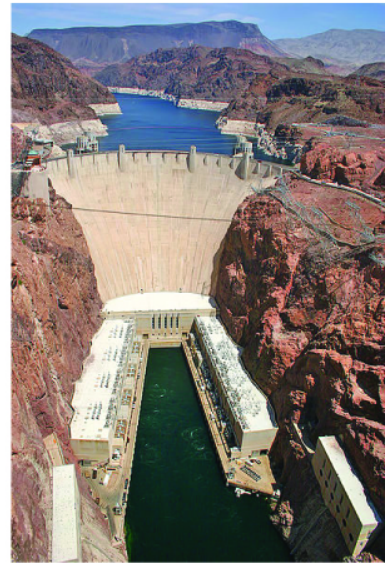
(a)   (b)

(a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. **Temperature** is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the

object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" ([link]). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.
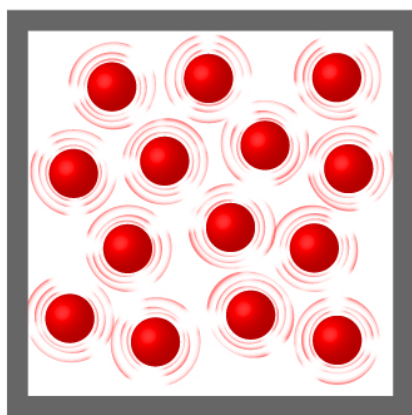
Hot water   Cold water
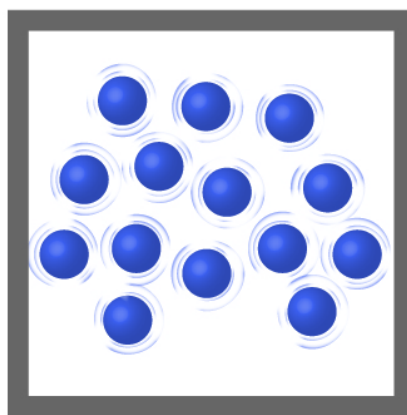
(a)   (b)

(a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Note:

Click on this [interactive simulation](link) to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in [link]. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.
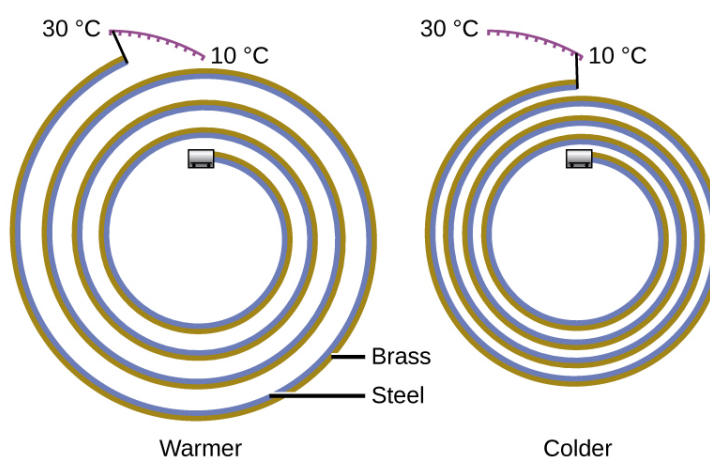
(a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass)

expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr)

Heat (*q*) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature ([link]).
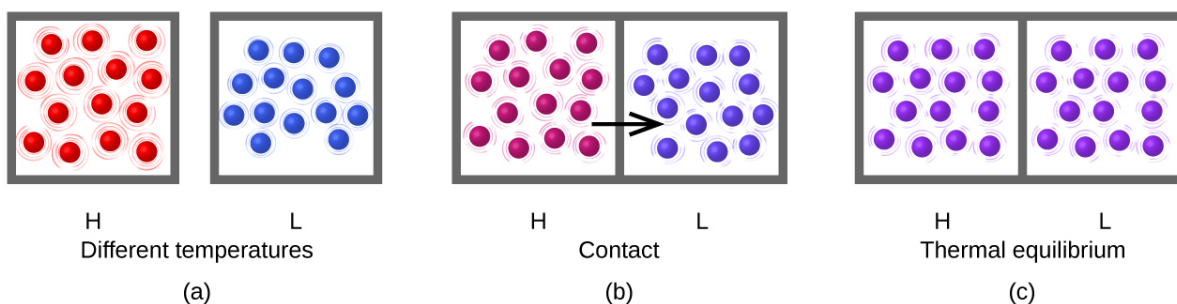
(a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Note:

Click on the PhET simulation to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**.

For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame ([link]). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

(a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons)

Historically, energy was measured in units of **calories (cal)**. A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The

Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A **joule (J)** is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity (C)** of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):
Equation:

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:
Equation:

$$C_{\text{small pan}} = \frac{18{,}140 \text{ J}}{50.0 \text{ °C}} = 363 \text{ J/°C}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a

(proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

Equation:

$$C_{\text{large pan}} = \frac{90{,}700 \text{ J}}{50.0 \text{ °C}} = 1814 \text{ J/°C}$$

The **specific heat capacity (c)** of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

Equation:

$$c = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

Equation:

$$c_{\text{iron}} = \frac{18{,}140 \text{ J}}{(808 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

Equation:

$$c_{\text{iron}} = \frac{90{,}700 \text{ J}}{(4040 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat

(for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C ([link]).

Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in [link].

Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (*state*)	Specific Heat (J/g °C)
helium	He(*g*)	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	Al(*s*)	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	Ar(*g*)	0.522
iron	Fe(*s*)	0.449
copper	Cu(*s*)	0.385
lead	Pb(*s*)	0.130
gold	Au(*s*)	0.129
silicon	Si(*s*)	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

Equation:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read "delta T") is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example:
Measuring Heat
A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution
To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1

°C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

Equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Equation:

$$\begin{aligned}
&= (4.184 \text{ J}/\cancel{\text{g}} \; ^\circ\text{C}) \times (800 \; \cancel{\text{g}}) \times (85 - 20) \; ^\circ\text{C} \\
&= (4.184 \text{ J}/\cancel{\text{g}} \; ^\circ\cancel{\text{C}}) \times (800 \; \cancel{\text{g}}) \times (65) \; ^\circ\cancel{\text{C}} \\
&= 210{,}000 \text{ J} \; (= 210 \text{ kJ})
\end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive.

Check Your Learning

How much heat, in joules, must be added to a 5.00×10^2-g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Note:
Answer:
5.05×10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example:
Determining Other Quantities
A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).
Solution
Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:
Equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:
Equation:

$$6640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) \, ^\circ\text{C}$$

Solving:
Equation:

$$c = \frac{6640 \text{ J}}{(348 \text{ g}) \times (21.2 \, ^\circ\text{C})} = 0.900 \text{ J/g} \, ^\circ\text{C}$$

Comparing this value with the values in [link], this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.
Check Your Learning
A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Note:
Answer:
c = 0.45 J/g °C; the metal is likely to be iron

Note:

Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) ([link]). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.
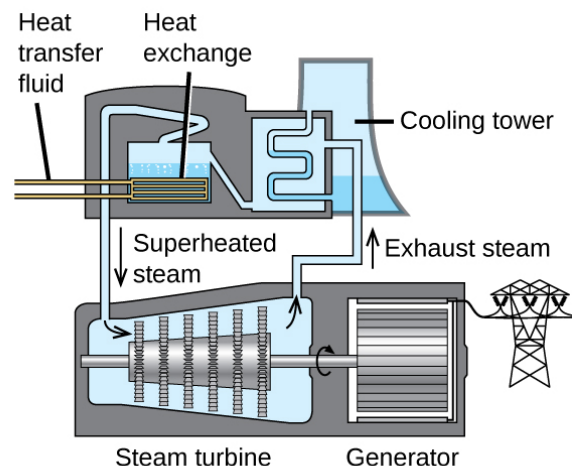
(a)   (b)

This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land

Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world ([link]). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.

(a)

(b)

(a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

Key Concepts and Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted

from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics).

Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J).

Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times \left(T_{\text{final}} - T_{\text{initial}} \right)$

Chemistry End of Chapter Exercises

Exercise:

Problem:

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

Solution:

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which

is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

Exercise:

Problem:

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

Exercise:

Problem:

Explain the difference between heat capacity and specific heat of a substance.

Solution:

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

Exercise:

Problem:

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 28.4 g of water

(b) 1.00 oz of lead

Exercise:

Problem:

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 45.8 g of nitrogen gas

(b) 1.00 pound of aluminum metal

Solution:

(a) 47.6 J/°C; 11.38 cal °C^{-1}; (b) 407 J/°C; 97.3 cal °C^{-1}

Exercise:

Problem:

How much heat, in joules and in calories, must be added to a 75.0–g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

Exercise:

Problem:

How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from −23.0 °C to −1.0 °C?

Solution:

1310; 313 cal

Exercise:

Problem:

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

Exercise:

Problem:

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

Solution:

7.15 °C

Exercise:

  Problem:

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

(a) What is the specific heat of the substance?

(b) If it is one of the substances found in [link], what is its likely identity?

Exercise:

  Problem:

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

(a) What is the specific heat of the substance?

(b) If it is one of the substances found in [link], what is its likely identity?

  Solution:

  (a) 0.390 J/g °C; (b) Copper is a likely candidate.

Exercise:

  Problem: An aluminum kettle weighs 1.05 kg.

(a) What is the heat capacity of the kettle?

(b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?

(c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific

heat of 4.184 J/g °C)?

Exercise:

Problem:

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) $= 3.6 \times 10^6$ J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield "positive" or "negative" errors)?

Solution:

We assume that the density of water is 1.0 g/cm^3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. Energy required = 7.47 kWh

Glossary

calorie (cal)
    unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process
    chemical reaction or physical change that absorbs heat

energy
    capacity to supply heat or do work

exothermic process
    chemical reaction or physical change that releases heat

heat (*q*)

   transfer of thermal energy between two bodies

heat capacity (*C*)

   extensive property of a body of matter that represents the quantity of
   heat required to increase its temperature by 1 degree Celsius (or 1
   kelvin)

joule (J)

   SI unit of energy; 1 joule is the kinetic energy of an object with a mass
   of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1
   kg m^2/s and 4.184 J = 1 cal

kinetic energy

   energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where *m* = mass
   and *v* = velocity)

potential energy

   energy of a particle or system of particles derived from relative
   position, composition, or condition

specific heat capacity (*c*)

   intensive property of a substance that represents the quantity of heat
   required to raise the temperature of 1 gram of the substance by 1
   degree Celsius (or 1 kelvin)

temperature

   intensive property of matter that is a quantitative measure of "hotness"
   and "coldness"

thermal energy

   kinetic energy associated with the random motion of atoms and
   molecules

thermochemistry

   study of measuring the amount of heat absorbed or released during a
   chemical reaction or a physical change

work (*w*)

    energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

Calorimetry
By the end of this section, you will be able to:

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as **calorimetry**. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a **system** (the substance or substances undergoing the chemical or physical change) and its **surroundings** (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature ([link]). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.
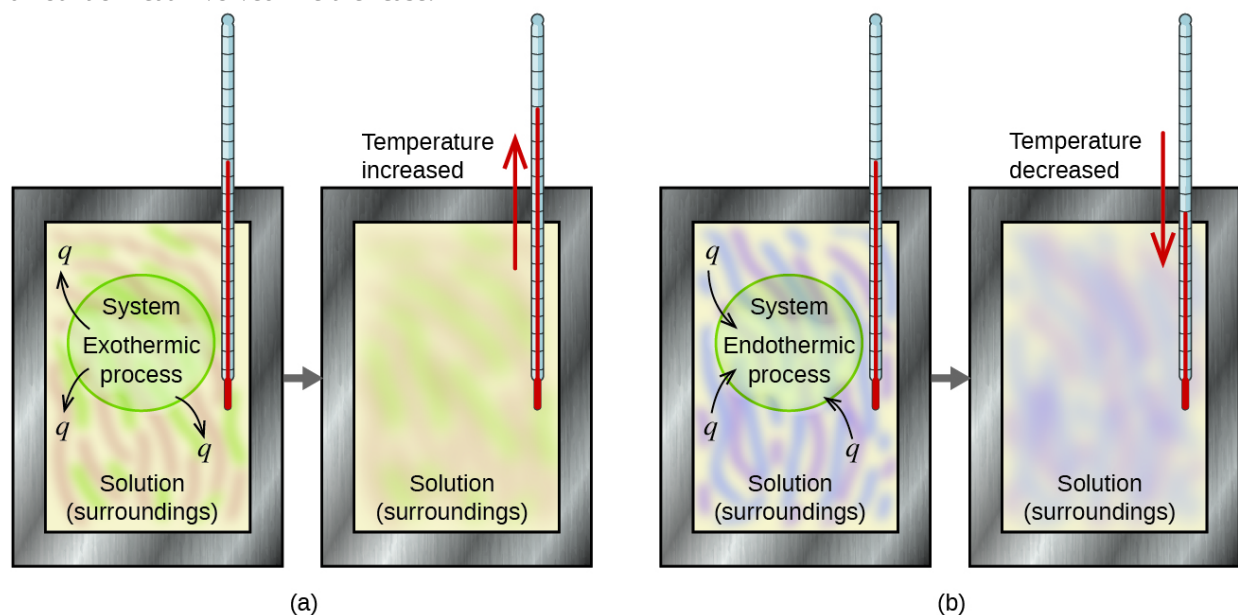
In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from

polystyrene cups ([link]). These easy-to-use "coffee cup" calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.
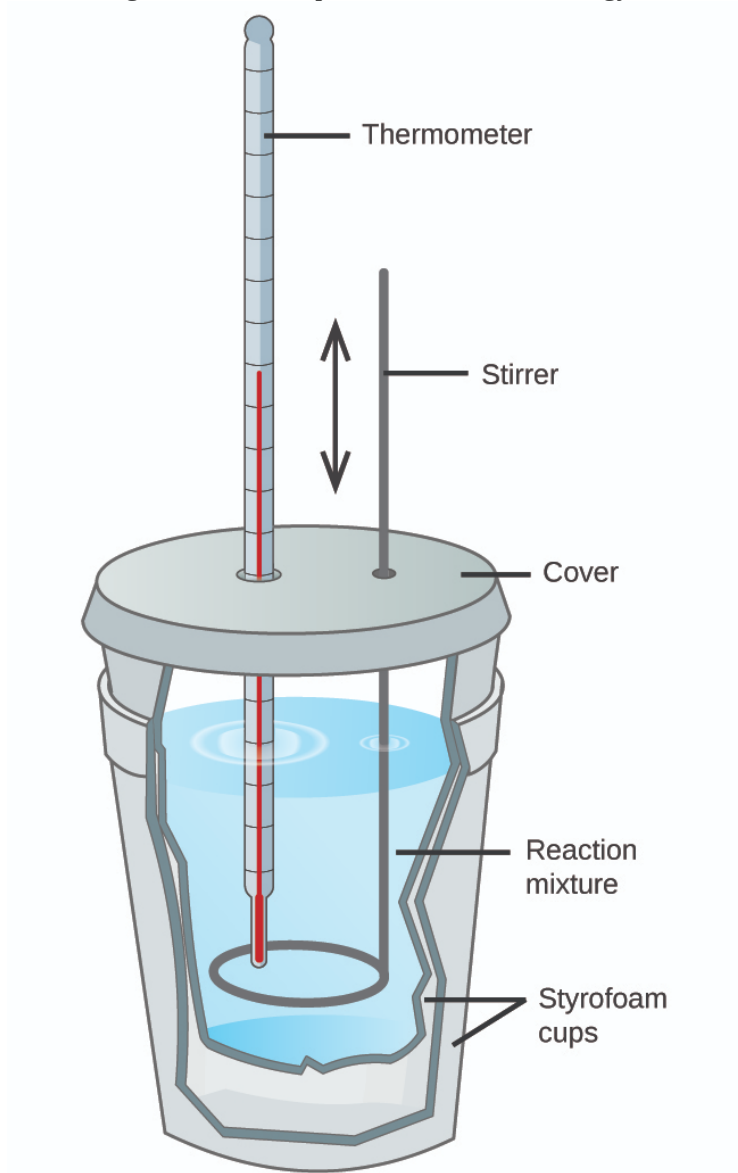
A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor ([link]).
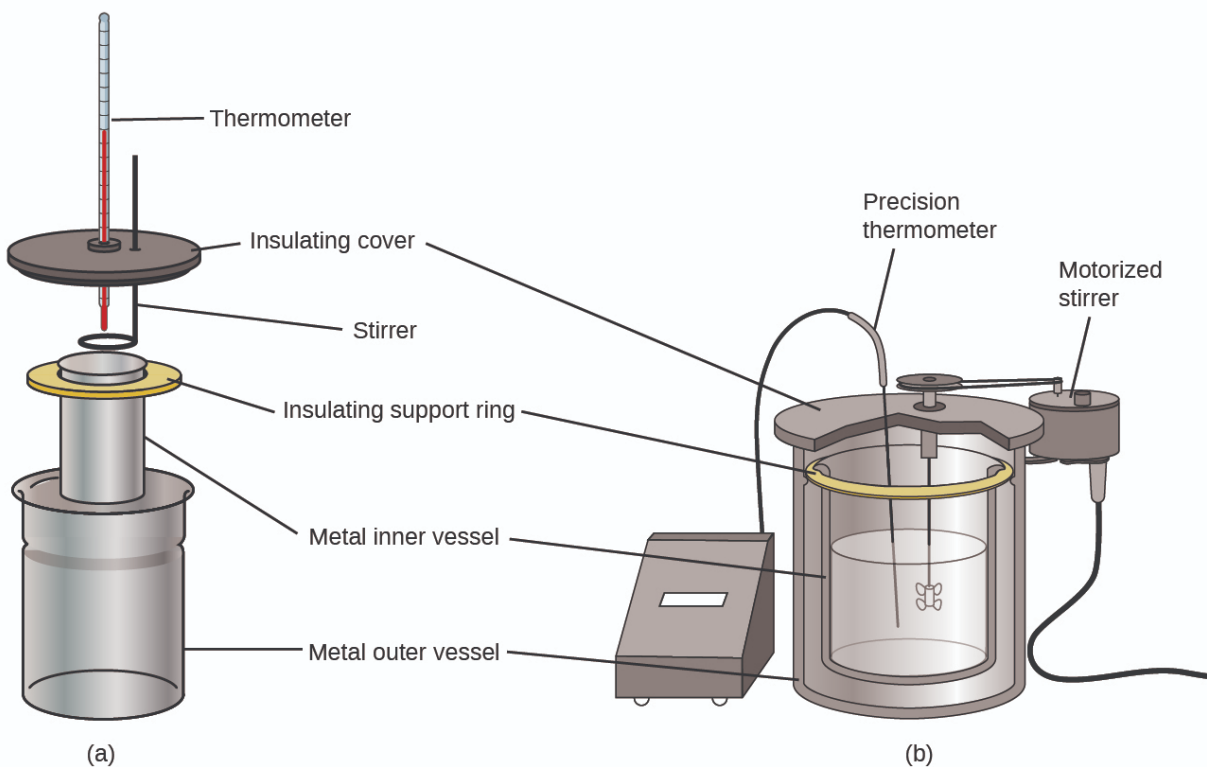
Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium ([link]). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

Equation:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

Equation:

$$q_{\text{substance M}} = -q_{\text{substance W}}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{\text{substance M}}$ and $q_{\text{substance W}}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat,

per definition). In the specific situation described, $q_{\text{substance M}}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.
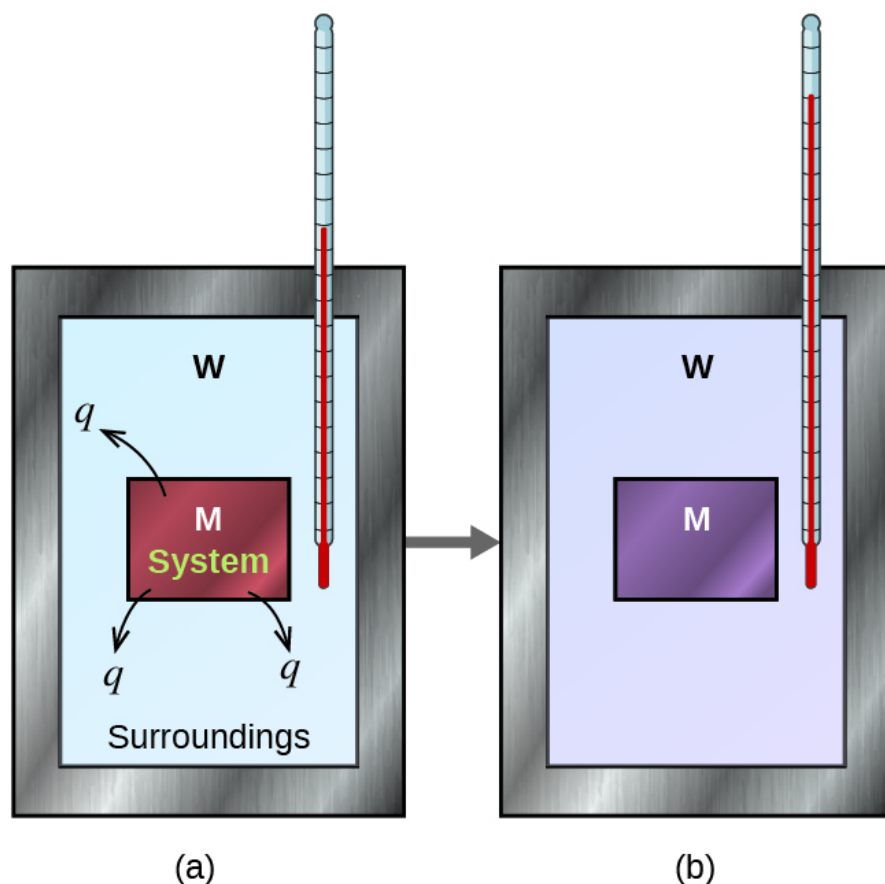
In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example:
Heat Transfer between Substances at Different Temperatures
A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron ([link]), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).
Solution
The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then *heat given off by rebar* = −*heat taken in by water*, or:
Equation:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:
Equation:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

Equation:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

Equation:

$$(0.449 \text{ J/g } ^{\circ}\text{C})(360 \text{ g})(42.7 \text{ }^{\circ}\text{C} - T_{\text{i,rebar}}) = (4.184 \text{ J/g } ^{\circ}\text{C})(425\text{g})(42.7 \text{ }^{\circ}\text{C} - 24.0 \text{ }^{\circ}\text{C})$$

Equation:

$$T_{i,rebar} = \frac{(4.184 \text{ J/g } ^{\circ}\text{C})(425 \text{ g})(42.7 \text{ }^{\circ}\text{C} - 24.0 \text{ }^{\circ}\text{C})}{(0.449 \text{ J/g } ^{\circ}\text{C})(360 \text{ g})} + 42.7 \text{ }^{\circ}\text{C}$$

Solving this gives $T_{\text{i,rebar}}$= 248 °C, so the initial temperature of the rebar was 248 °C.

Check Your Learning
A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Note:
Answer:
The initial temperature of the copper was 335.6 °C.

Check Your Learning
A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Note:
Answer:
The final temperature (reached by both copper and water) is 38.8 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example:
Identifying a Metal by Measuring Specific Heat
A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.
Solution

Assuming perfect heat transfer, *heat given off by metal = −heat taken in by water*, or:

Equation:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

Equation:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i, metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

Equation:

$$(c_{\text{metal}})(59.7\,\text{g})(28.5\,^\circ\text{C} - 100.0\,^\circ\text{C}) = -(4.18\,\text{J/g}\,^\circ\text{C})(60.0\,\text{g})(28.5\,^\circ\text{C} - 22.0\,^\circ\text{C})$$

Solving this:

Equation:

$$c_{\text{metal}} = \frac{-(4.184\,\text{J/g}\,^\circ\text{C})(60.0\,\text{g})(6.5\,^\circ\text{C})}{(59.7\,\text{g})(-71.5\,^\circ\text{C})} = 0.38\,\text{J/g}\,^\circ\text{C}$$

Comparing this with values in [link], our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Check Your Learning

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Note:
Answer:

$c_{\text{metal}} = 0.13$ J/g °C
This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution}, must add up to zero:

Equation:

$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

Equation:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

This concept lies at the heart of all calorimetry problems and calculations.

Note:

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands ([link]). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $NaC_2H_3O_2(aq) \longrightarrow NaC_2H_3O_2(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused.

Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is $2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s)$. Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

Note:

This link shows the precipitation reaction that occurs when the disk in a chemical hand warmer is flexed.

Example:

Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an "instant ice pack" ([link]). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of q for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.

An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

Equation:

$$q_{rxn} = -q_{soln}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

Equation:

$$q_{rxn} = -q_{soln} = -(\,c \times m \times \Delta T)_{soln}$$
$$= -[(4.184 \text{ J/g }°\text{C}) \times (53.2 \text{ g}) \times (20.3\ °\text{C} - 24.9\ °\text{C})]$$
$$= -[(4.184 \text{ J/g }°\text{C}) \times (53.2 \text{ g}) \times (-4.6\ °\text{C})]$$
$$+1.0 \times 10^3 \text{ J} = +1.0 \text{ kJ}$$

The positive sign for q indicates that the dissolution is an endothermic process.

Check Your Learning

When a 3.00-g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Note:
Answer:

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a **bomb calorimeter**, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water ([link]). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is trapped in the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.
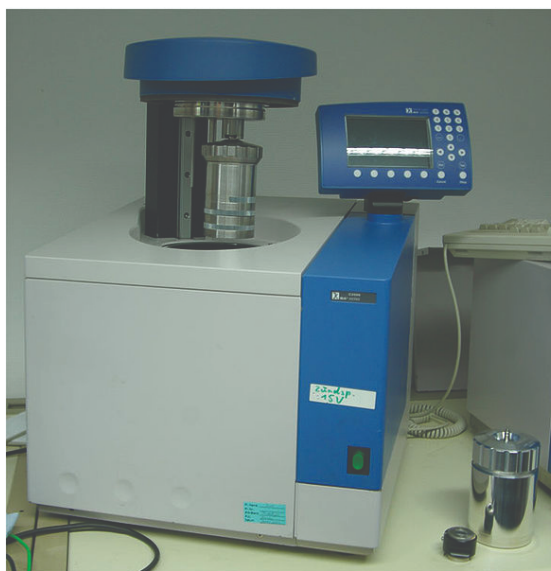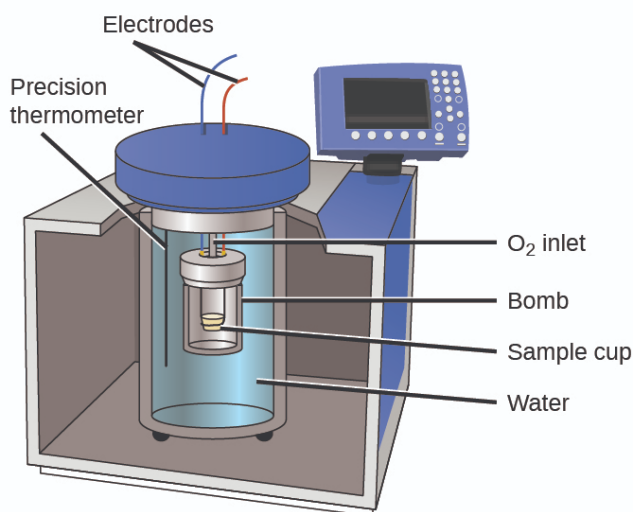
(a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

> **Note:**
>
>
>
> Click on this link to view how a bomb calorimeter is prepared for action.

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[footnote] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A **nutritional calorie (Calorie)** is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, http://link.springer.com/article/10.1007/s11517-006-0086-5.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients ([link]).

(a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:
Equation:

$$(5 \, \text{g protein} \, \times \, 4 \, \text{Calories/g}) + (31 \, \text{g carb} \, \times \, 4 \, \text{Calories/g}) + (12 \, \text{g fat} \, \times \, 9 \, \text{Calories/g}) = 252 \, \text{Calories}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate,

protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Key Concepts and Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations.

Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Chemistry End of Chapter Exercises

Exercise:

  Problem:

  A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.

Exercise:

  Problem:

  Would the amount of heat measured for the reaction in [link] be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

  Solution:

  lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

Exercise:

Problem:

Would the amount of heat absorbed by the dissolution in [link] appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

Exercise:

Problem:

How many milliliters of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

Exercise:

Problem:

How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

Solution:

The temperature of the coffee will drop 1 degree.

Exercise:

Problem:

A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in [link]. The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?

Exercise:

Problem:

A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter ([link]). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Exercise:

Problem:

Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter ([link]) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Solution:

2.2 kJ; The heat produced shows that the reaction is exothermic.

Exercise:

Problem:

The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g?

Solution:

30%

Exercise:

Problem:

A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?

Exercise:

Problem:

A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

Solution:

1.4×10^2 Calories

Glossary

bomb calorimeter
    device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

calorimeter
    device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry
    process of measuring the amount of heat involved in a chemical or physical process

nutritional calorie (Calorie)
    unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

surroundings
    all matter other than the system being studied

system
    portion of matter undergoing a chemical or physical change being studied

Enthalpy
By the end of this section, you will be able to:

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of **chemical thermodynamics**, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the **internal energy (U)**, sometimes symbolized as E.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (q) from the surroundings or when the surroundings do work (w) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:
Equation:

$$\Delta U = q + w$$

as shown in [link]. This is one version of the **first law of thermodynamics**, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.
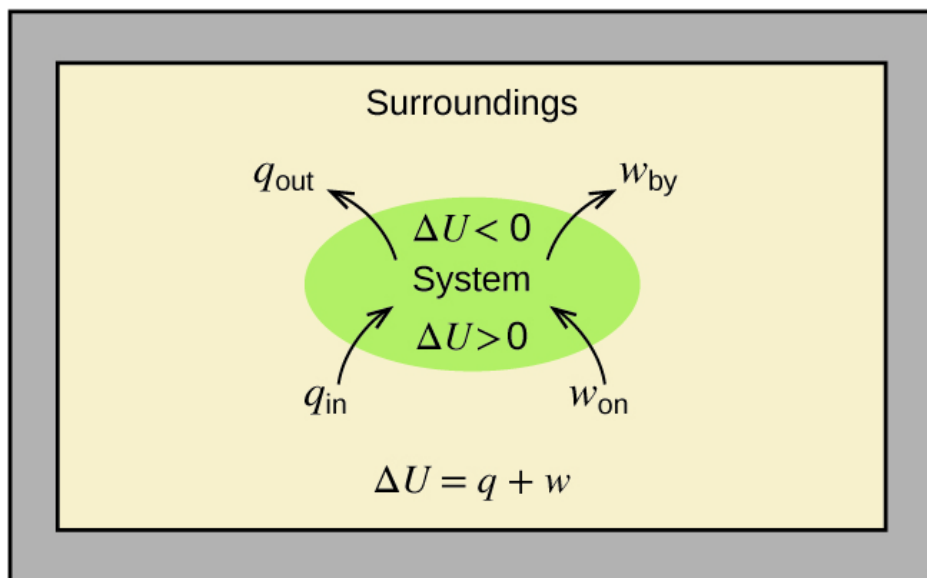
The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called **expansion work** (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

Note:

This view of an internal combustion engine illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a **state function** (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path ([link]). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).
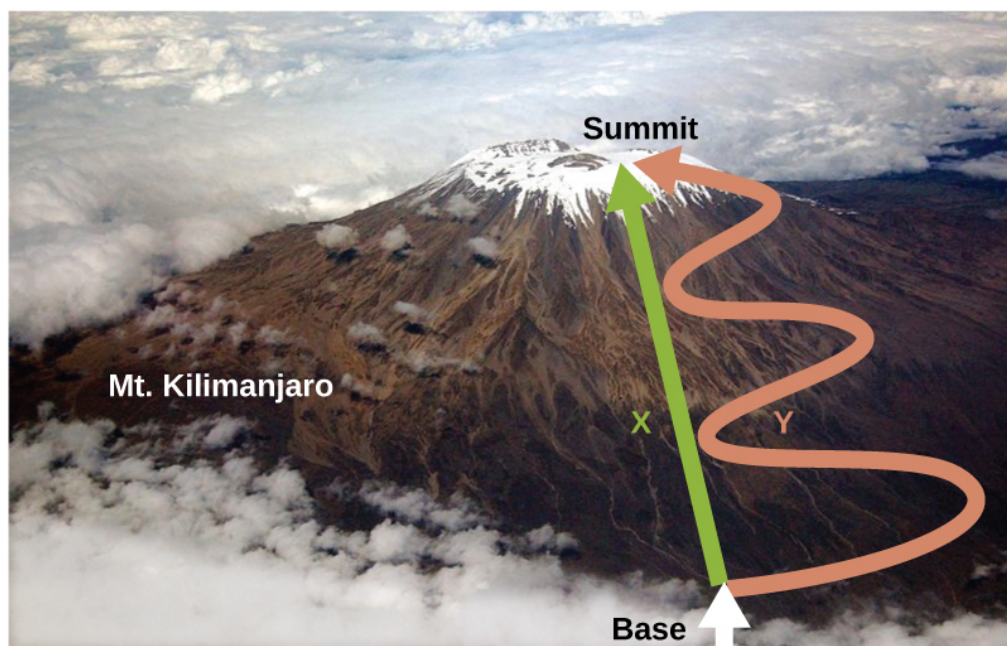
Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Chemists ordinarily use a property known as **enthalpy (H)** to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (U) and the mathematical product of its pressure (P) and volume (V):
Equation:

$$H = U + PV$$

Since it is derived from three state functions (U, P, and V), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the **enthalpy change (ΔH)** is:
Equation:

$$\Delta H = \Delta U + P\Delta V$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will always be opposite:

Equation:

$$P\Delta V = -w$$

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

Equation:

$$\Delta H = \Delta U + P\Delta V$$
$$= q_\mathrm{p} + w - w$$
$$= q_\mathrm{p}$$

where q_p is the heat of reaction under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter ([link]) is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:
   Equation:

$$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l) \qquad \Delta H = -286\,\mathrm{kJ}$$
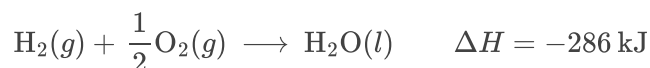
   This equation indicates that when 1 mole of hydrogen gas and $\frac{1}{2}$ mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):
   Equation:

(two-fold increase in amounts)

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = 2 \times (-286\,\text{kJ}) = -572\,\text{kJ}$$

(two-fold decrease in amounts)

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{4}O_2(g) \longrightarrow \tfrac{1}{2}H_2O(l) \qquad \Delta H = \tfrac{1}{2} \times (-286\,\text{kJ}) = -143\,\text{kJ}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and $\frac{1}{2}$ mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.
   Equation:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -242\,\text{kJ}$$
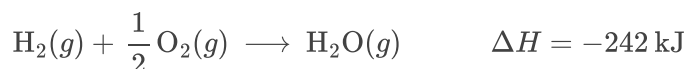
3. A negative value of an enthalpy change, ΔH, indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A **standard state** is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol (ΔH°_{298}) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH°_C) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat

produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.
Equation:

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2 + 3H_2O(l) \qquad \Delta H_{298}^{\circ} = -1366.8 \text{ kJ}$$
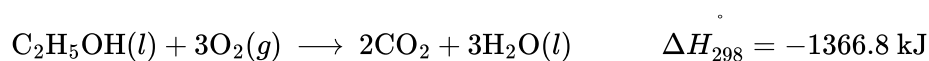
Enthalpies of combustion for many substances have been measured; a few of these are listed in [link]. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and **hydrocarbons** (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Standard Molar Enthalpies of Combustion		
Substance	**Combustion Reaction**	**Enthalpy of Combustion, ΔH_c°** ($\frac{\text{kJ}}{\text{mol}}$ at 25 $^{\circ}$C)
carbon	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5
hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	−601.6
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	−296.8
carbon monoxide	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	−283.0
methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−890.8
acetylene	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	−1301.1
ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1366.8
methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$	−5461

Note:
Emerging Algae-Based Energy Technologies (Biofuels)
As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae

([link]). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.
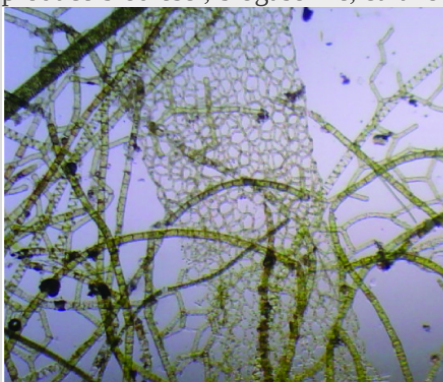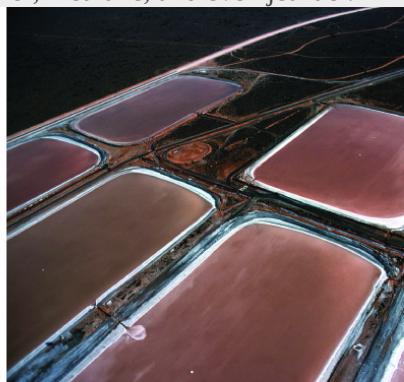
(a)   (b)   (c)

(a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon.[footnote] The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute ([link]).

For more on algal fuel, see http://www.theguardian.com/environment/2010/feb/13/algae-solve-pentagon-fuel-problem.

Grow → Harvest → Extract → Process and purify → Jet fuel Gasoline Diesel
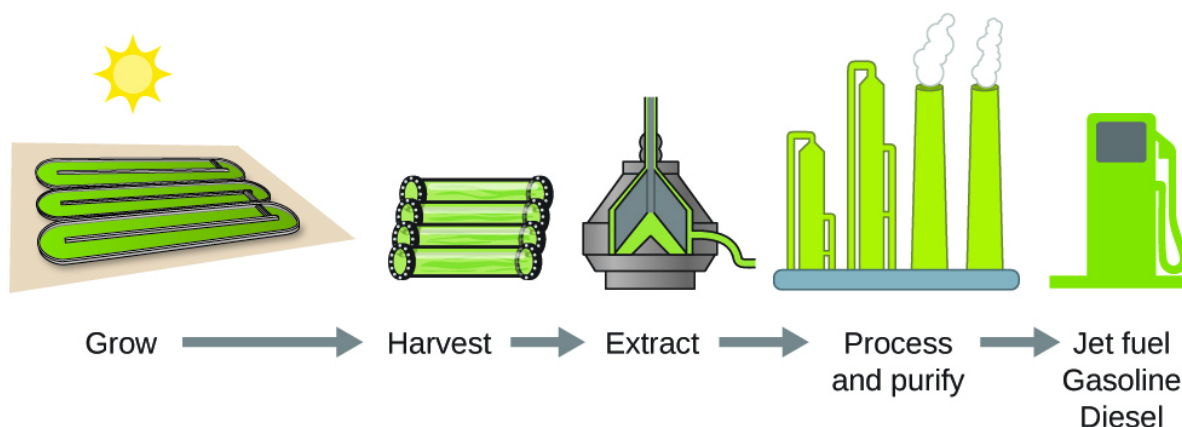
Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Standard Enthalpy of Formation

A **standard enthalpy of formation** ΔH_f° is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is -393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:
Equation:

$$\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) \qquad \Delta H_f^\circ = \Delta H_{298}^\circ = -393.5 \text{ kJ}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C.

For nitrogen dioxide, $NO_2(g)$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:
Equation:

$$\frac{1}{2}\mathrm{N}_2(g) + \mathrm{O}_2(g) \longrightarrow \mathrm{NO}_2(g) \qquad \Delta H_f^\circ = \Delta H_{298}^\circ = +33.2 \text{ kJ}$$
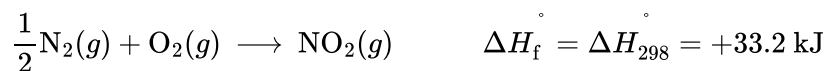
A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Appendix G. These values indicate that formation reactions range from highly exothermic (such as -2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as $+226.7$ kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Evaluating an Enthalpy of Formation

Ozone, $O_3(g)$, forms from oxygen, $O_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

Equation:

$$3O_2(g) \longrightarrow 2O_3(g) \qquad \Delta H_{298}^\circ = +286 \text{ kJ}$$
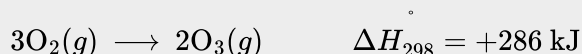
Solution

ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for $O_3(g)$ is the enthalpy change for the reaction:

Equation:

$$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$$
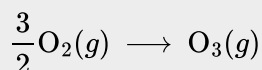
For the formation of 2 mol of $O_3(g)$, $\Delta H_{298}^\circ = +286$ kJ. This ratio, $\left(\frac{286 \text{ kJ}}{2 \text{ mol } O_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

Equation:

$$\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1 \; \cancel{\text{mol } O_3} \times \frac{286 \text{ kJ}}{2 \; \cancel{\text{mol } O_3}} = 143 \text{ kJ}$$

Therefore, $\Delta H_f^\circ [O_3(g)] = +143$ kJ/mol.

Check Your Learning

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, $HCl(g)$. What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $HCl(g)$ is −92.3 kJ/mol.

Note:
Answer:

For the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H_{298}^\circ = -184.6$ kJ

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of **Hess's law**, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps*. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:
Equation:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ_{298} = -394\,\text{kJ}$$
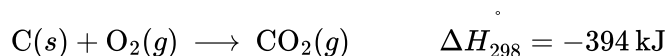
In the two-step process, first carbon monoxide is formed:
Equation:

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H^\circ_{298} = -111\,\text{kJ}$$
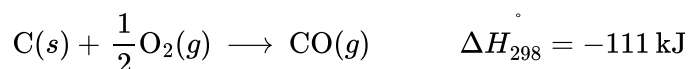
Then, carbon monoxide reacts further to form carbon dioxide:
Equation:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ_{298} = -283\,\text{kJ}$$
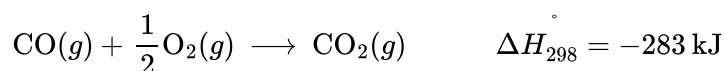
The equation describing the overall reaction is the sum of these two chemical changes:
Equation:

$$\text{Step 1: } C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)$$
$$\text{Step 2: } CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$$
$$\text{Sum: } C(s) + \tfrac{1}{2}O_2(g) + CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) + CO_2(g)$$
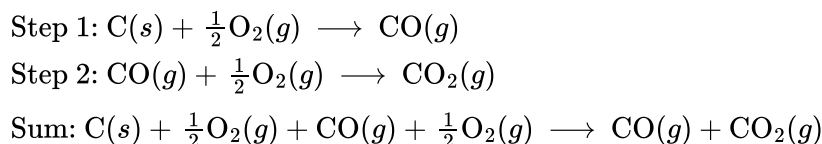
Because the CO produced in Step 1 is consumed in Step 2, the net change is:
Equation:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
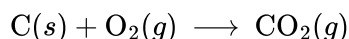
According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in [link] to find the enthalpy change of the entire reaction from its two steps:
Equation:

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H^\circ_{298} = -111\,\text{kJ}$$
$$\frac{CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)}{C(s) + O_2(g) \longrightarrow CO_2(g)} \qquad \frac{\Delta H^\circ_{298} = -283\,\text{kJ}}{\Delta H^\circ_{298} = -394\,\text{kJ}}$$
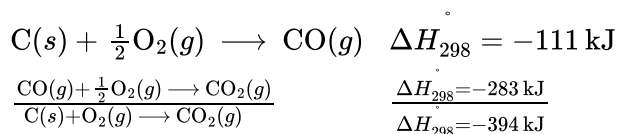
The result is shown in [link]. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.
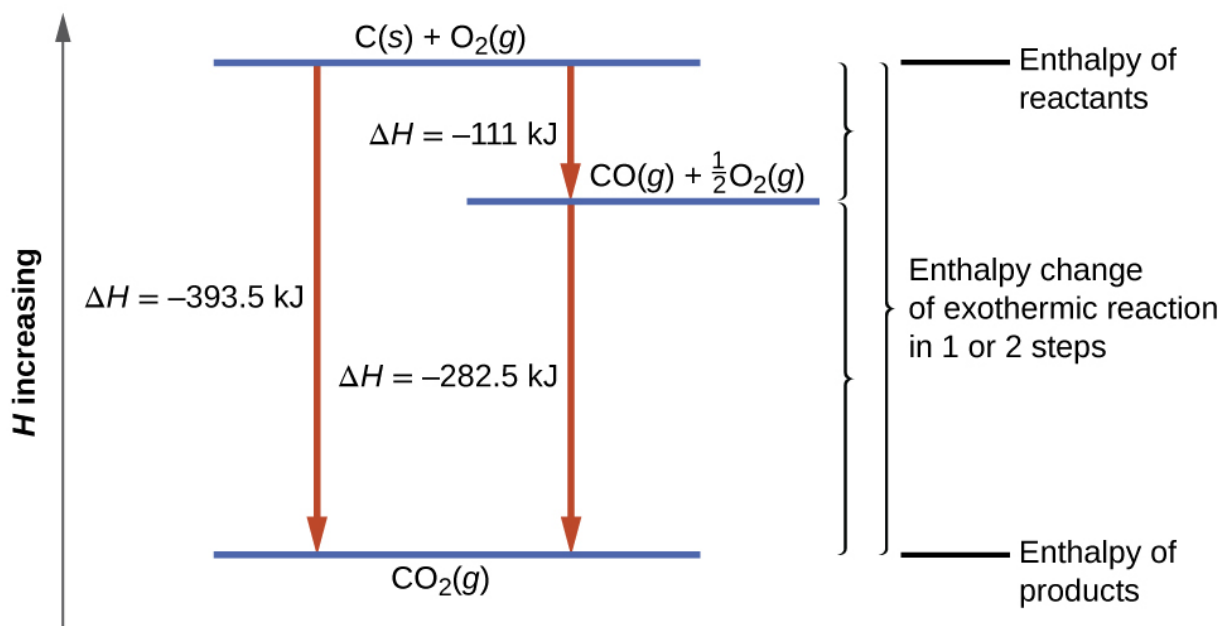
The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:
   Equation:

   $$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = +33.2 \text{ kJ}$$
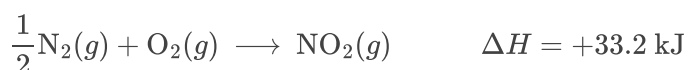
   When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:
   Equation:

   $$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = +66.4 \text{ kJ}$$
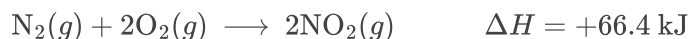
   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:
   Equation:

   $$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -184.6 \text{ kJ}$$
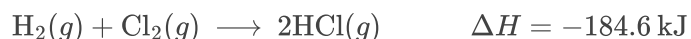
Then, for the "reverse" reaction, the enthalpy change is also "reversed":
Equation:

$$2\text{HCl}(g) \longrightarrow \text{H}_2(g) + \text{Cl}_2(g) \qquad \Delta H = +184.6 \text{ kJ}$$
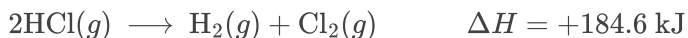
Example:

Stepwise Calculation of $\Delta H_\text{f}^{\circ}$ Using Hess's Law

Determine the enthalpy of formation, $\Delta H_\text{f}^{\circ}$, of FeCl$_3$(s) from the enthalpy changes of the following two-step process that occurs under standard state conditions:
Equation:

$$\text{Fe}(s) + \text{Cl}_2(g) \longrightarrow \text{FeCl}_2(s) \qquad \Delta H^{\circ} = -341.8 \text{ kJ}$$

Equation:

$$\text{FeCl}_2(s) + \frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{FeCl}_3(s) \qquad \Delta H^{\circ} = -57.7 \text{ kJ}$$
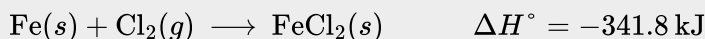
Solution
We are trying to find the standard enthalpy of formation of FeCl$_3$(s), which is equal to ΔH° for the reaction:
Equation:

$$\text{Fe}(s) + \frac{3}{2}\text{Cl}_2(g) \longrightarrow \text{FeCl}_3(s) \qquad \Delta H_\text{f}^{\circ} =?$$
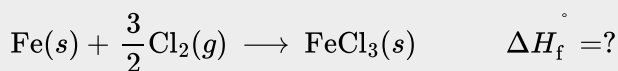
Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their ΔHs:
Equation:

$$\text{Fe}(s) + \text{Cl}_2(g) \longrightarrow \text{FeCl}_2(s) \qquad \Delta H^{\circ} = -341.8 \text{ kJ}$$
$$\frac{\text{FeCl}_2(s) + \frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{FeCl}_3(s)}{\text{Fe}(s) + \frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{FeCl}_3(s)} \qquad \frac{\Delta H^{\circ} = -57.7 \text{ kJ}}{\Delta H^{\circ} = -399.5 \text{ kJ}}$$
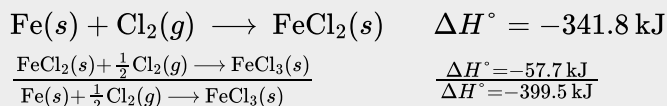
The enthalpy of formation, $\Delta H_\text{f}^{\circ}$, of FeCl$_3$(s) is −399.5 kJ/mol.
Check Your Learning
Calculate ΔH for the process:
Equation:

$$\text{N}_2(g) + 2\text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$$

from the following information:
Equation:

$$\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g) \qquad \Delta H = 180.5 \text{ kJ}$$
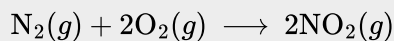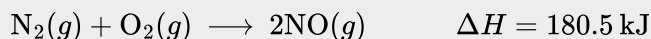
Equation:
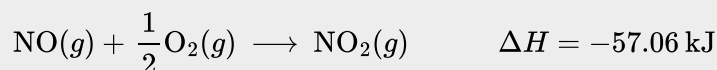
$$\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}_2(g) \qquad \Delta H = -57.06 \text{ kJ}$$

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and n standing for the stoichiometric coefficients:
Equation:

$$\Delta H^{\circ}_{\text{reaction}} = \sum n \times \Delta H^{\circ}_{\text{f}} (\text{products}) - \sum n \times \Delta H^{\circ}_{\text{f}} (\text{reactants})$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example:
Using Hess's Law
What is the standard enthalpy change for the reaction:
Equation:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g) \qquad \Delta H^{\circ} = ?$$
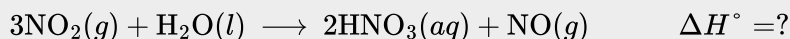
Solution: Using the Equation
Use the special form of Hess's law given previously:
Equation:

$$\Delta H^{\circ}_{\text{reaction}} = \sum n \times \Delta H^{\circ}_{\text{f}} (\text{products}) - \sum n \times \Delta H^{\circ}_{\text{f}} (\text{reactants})$$

Equation:

$$= \left[2 \cancel{\text{mol HNO}_3} \times \frac{-207.4\,\text{kJ}}{\cancel{\text{mol HNO}_3(aq)}} + 1 \cancel{\text{mol NO}(g)} \times \frac{+90.2\,\text{kJ}}{\cancel{\text{mol NO}(g)}} \right]$$

$$- \left[3 \cancel{\text{mol NO}_2(g)} \times \frac{+33.2\,\text{kJ}}{\cancel{\text{mol NO}_2(g)}} + 1 \cancel{\text{mol H}_2\text{O}(l)} \times \frac{-285.8\,\text{kJ}}{\cancel{\text{mol H}_2\text{O}(l)}} \right]$$

$$= 2\,(-207.4\,\text{kJ}) + 1(+90.2\,\text{kJ}) - 3\,(+33.2\,\text{kJ}) - 1\,(-285.8\,\text{kJ})$$

$$= -138.4\,\text{kJ}$$

Solution: Supporting Why the General Equation Is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\text{NO}_2(g)$ and $1\text{H}_2\text{O}(l)$ into their constituent elements, and the formation of $2\text{HNO}_3(aq)$ and $1\text{NO}(g)$ from their constituent elements.

Writing out these reactions, and noting their relationships to the ΔH_f° values for these compounds (from Appendix G), we have:

Equation:

$$3\text{NO}_2(g) \longrightarrow 3/2\text{N}_2(g) + 3\text{O}_2(g) \qquad \Delta H_1^{\circ} = -99.6\,\text{kJ}$$

Equation:

$$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \qquad \Delta H_2^{\circ} = +285.8\,\text{kJ}\,[-1 \times \Delta H_f^{\circ}(\text{H}_2\text{O})]$$

Equation:

$$\text{H}_2(g) + \text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow 2\text{HNO}_3(aq) \qquad \Delta H_3^{\circ} = -414.8\,\text{kJ}\,[2 \times \Delta H_f^{\circ}(\text{HNO}_3)]$$

Equation:

$$\frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}(g) \qquad \Delta H_4^{\circ} = +90.2\,\text{kJ}\,[1 \times (\text{NO})]$$
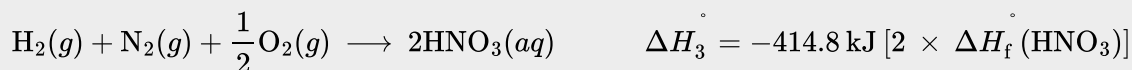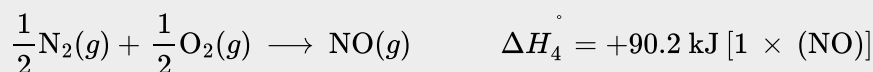
Summing these reaction equations gives the reaction we are interested in:
Equation:

$$3\text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2\text{HNO}_3(aq) + \text{NO}(g)$$
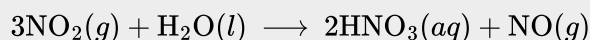
Summing their enthalpy changes gives the value we want to determine:
Equation:

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ} + \Delta H_4^{\circ} = (-99.6\,\text{kJ}) + (+285.8\,\text{kJ}) + (-414.8\,\text{kJ}) + (+90.2\,\text{kJ})$$
$$= -138.4\,\text{kJ}$$

So the standard enthalpy change for this reaction is $\Delta H^{\circ} = -138.4$ kJ.

Note that this result was obtained by (1) multiplying the ΔH_f° of each product by its stoichiometric coefficient and summing those values, (2) multiplying the ΔH_f° of each reactant by its stoichiometric coefficient and summing those values, and then (3) subtracting the result found in (2) from the result found in (1). This is also the procedure in using the general equation, as shown.

Check Your Learning

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, −278 kJ/mol; $H_2O(l)$, −286 kJ/mol; and $CO_2(g)$, −394 kJ/mol.

Note:
Answer:
−1368 kJ/mol

Key Concepts and Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or ΔH_{298}° for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH_f°, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

Key Equations

- $\Delta U = q + w$
- $\Delta H_{reaction}^{\circ} = \sum n \times \Delta H_f^{\circ} \left(\text{products} \right) - \sum n \times \Delta H_f^{\circ} \left(\text{reactants} \right)$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Although the gas used in an oxyacetylene torch ([link]) is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in [link]. Considering the conditions for which the tabulated data are reported, suggest an explanation.

Exercise:

Problem:

How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

Solution:

5204.4 kJ

Exercise:

  Problem:

  How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

  Solution:

  1.83×10^{-2} mol

Exercise:

  Problem:

  From the molar heats of formation in <u>Appendix G</u>, determine how much heat is required to evaporate one mole of water: $H_2O\,(l) \longrightarrow H_2O\,(g)$

  Solution:

  44.01 kJ/mol

Exercise:

  Problem: Calculate ΔH for the process $Hg_2Cl_2(s) \longrightarrow 2Hg\,(l) + Cl_2(g)$

  from the following information:
  $Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s) \qquad \Delta H = -224\,kJ$
  $Hg(l) + HgCl_2(s) \longrightarrow Hg_2Cl_2(s) \qquad \Delta H = -41.2\,kJ$
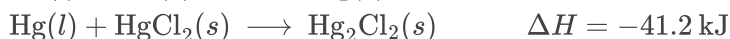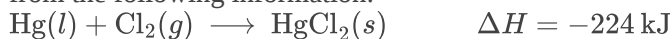
  Solution:

  265 kJ

Exercise:

  Problem:

  Using the data in <u>Appendix G</u>, calculate the standard enthalpy change for each of the following reactions:

  (a) $Si\,(s) + 2F_2(g) \longrightarrow SiF_4(g)$

  (b) $2C\,(s) + 2H_2(g) + O_2(g) \longrightarrow CH_3CO_2H\,(l)$

  (c) $CH_4(g) + N_2(g) \longrightarrow HCN\,(g) + NH_3(g);$

  (d) $Cs_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$
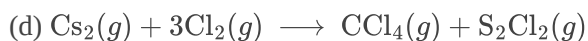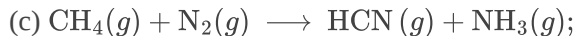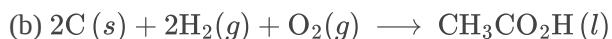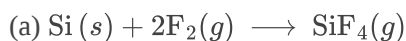
  Solution:

  (a) -1615.0 kJ mol^{-1}; (b) -484.3 kJ mol^{-1}; (c) 164.2 kJ; (d) -232.1 kJ

Exercise:

Problem:

The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in , determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

$$2H_2O_2(l) \longrightarrow 2H_2O(g) + O_2(g)$$

Solution:

-54.04 kJ mol^{-1}

Glossary

chemical thermodynamics
  area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (H)
  sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)
  heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)
  work done as a system expands or contracts against external pressure

first law of thermodynamics
  internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law
  if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon
  compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (U)
  total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion $\left(\Delta H_c^{\circ}\right)$
  heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation $\left(\Delta H_f^{\circ}\right)$
  enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state
  set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function
    property depending only on the state of a system, and not the path taken to reach that state

Introduction
class="introduction"

- Ionic Bonding
- Covalent Bonding
- Lewis Symbols and Structures
- Formal Charges and Resonance
- Strengths of Ionic and Covalent Bonds
- Molecular Structure and Polarity

Nicknamed "buckyballs," buckminsterfullerene molecules (C_{60}) contain only carbon atoms. Here they are shown in a ball-and-stick model (left). These molecules have single and double carbon-carbon bonds arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This unconventional molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to

create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by "Petey21"/Wikimedia Commons; credit right: modification of work by Bill Morrow)
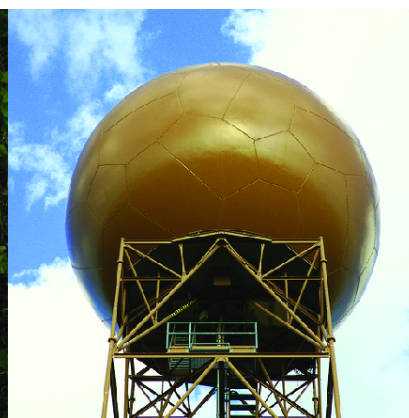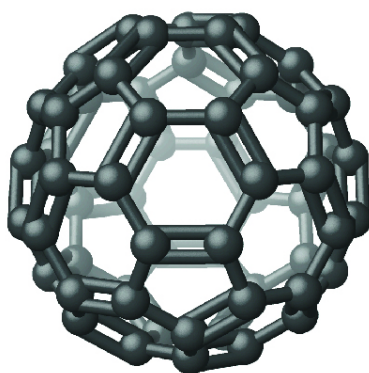
It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene, commonly known as a "buckyball." This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60}, and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.

Ionic Bonding
By the end of this section, you will be able to:

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by **ionic bonds**: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* ([link]). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.

(a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound

contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, $(2 \times +3) + (3 \times -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions ([link]).

(a)   (b)
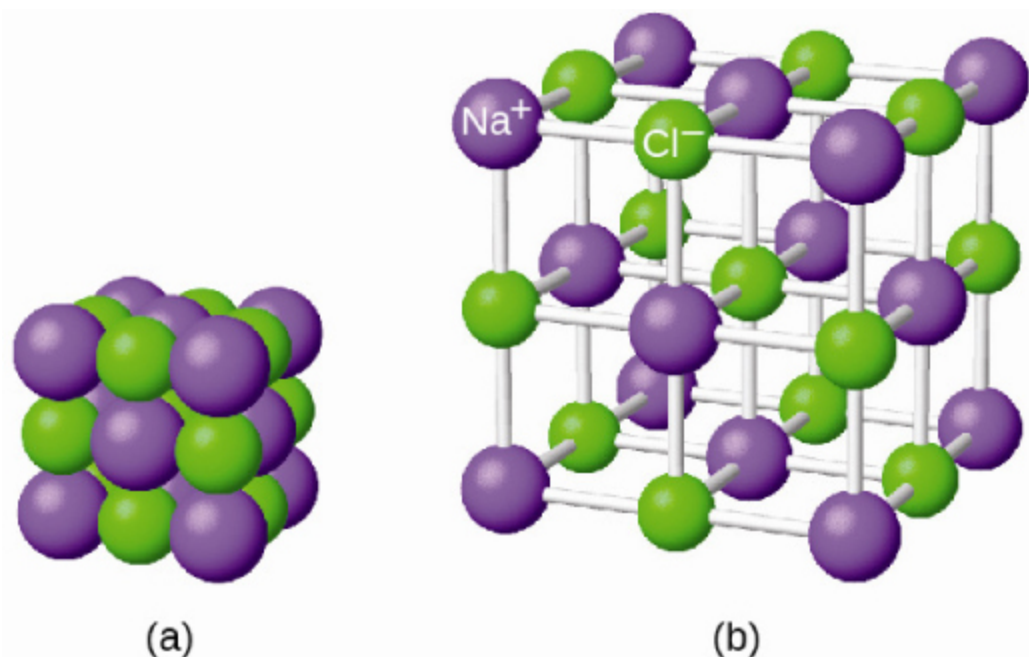
The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

Equation:

$$NaCl(\ ) \longrightarrow Na^+(\ ) + Cl^-(\ ) \qquad \Delta \quad = 769\,kJ$$

Key Concepts and Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Does a cation gain protons to form a positive charge or does it lose electrons?

Solution:

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

Exercise:

Problem:

Iron(III) sulfate [$Fe_2(SO_4)_3$] is composed of Fe^{3+} and $SO_4{}^{2-}$ ions. Explain why a sample of iron(III) sulfate is uncharged.

Exercise:

Problem:

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

Solution:

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

Exercise:

Problem:

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

Exercise:

Problem:

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) P

(b) Mg

(c) Al

(d) O

(e) Cl

(f) Cs

Solution:

(a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^-; (f) Cs^+

Exercise:

Problem:

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) I

(b) Sr

(c) K

(d) N

(e) S

(f) In

Exercise:

Problem:

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

Glossary

inert pair effect

tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

ionic bond
strong electrostatic force of attraction between cations and anions in an ionic compound

Covalent Bonding
By the end of this section, you will be able to:

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons equally between each other. Such bonds are called **covalent bonds**. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. [link] illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the x-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the x-axis), their valence orbitals (1s) begin to overlap.

The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The **bond length** is determined by the distance at which the lowest potential energy is achieved.

-7.24×10^{-19} J

Energy (J)

0

0.74

(H — H distance)

Internuclear distance (pm)
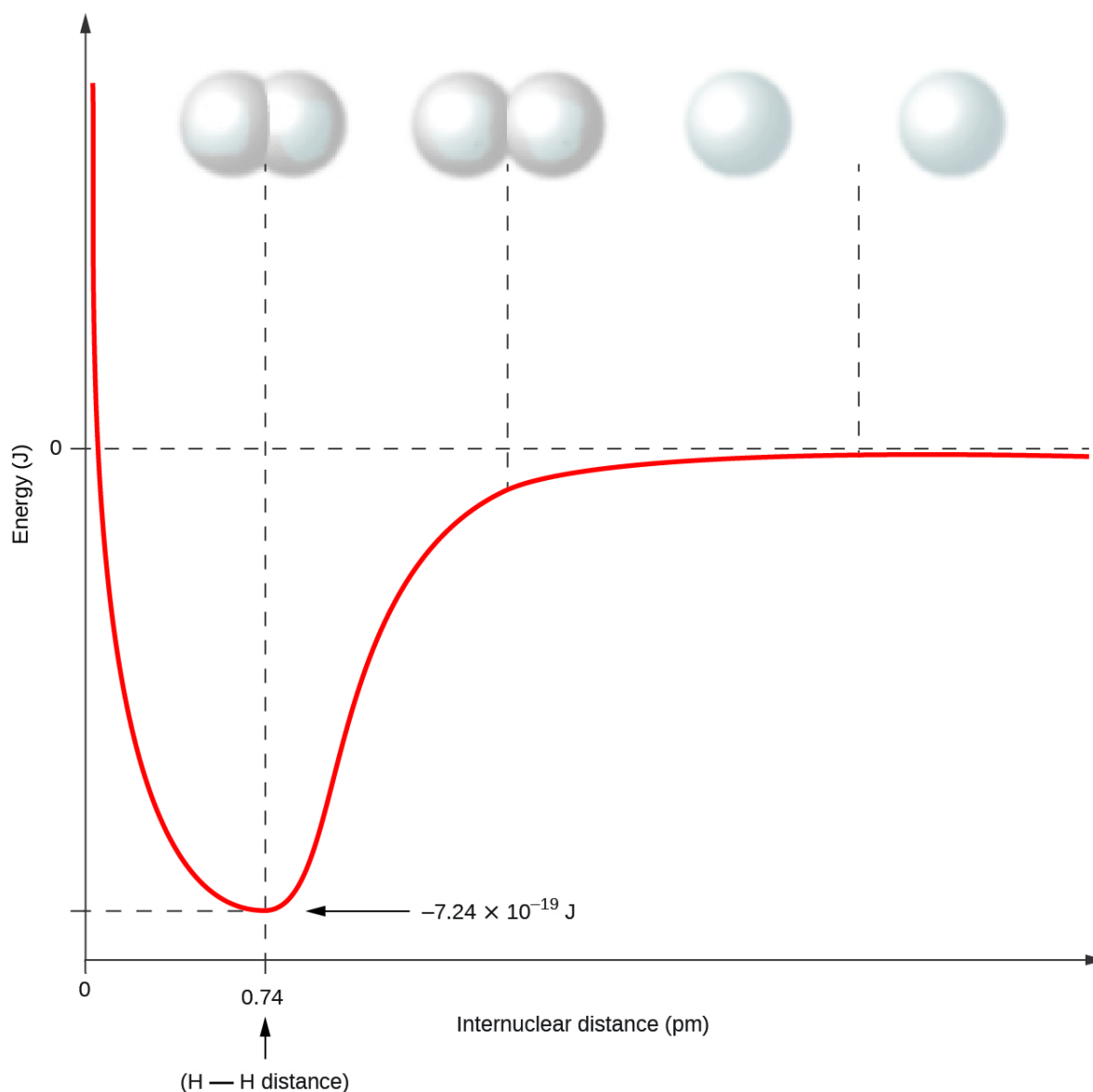
The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:
Equation:

$$H_2(g) \longrightarrow 2H(g) \qquad \Delta H = 436\,\text{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:
Equation:

$$2H(g) \longrightarrow H_2(g) \qquad \Delta H = -436\,\text{kJ}$$
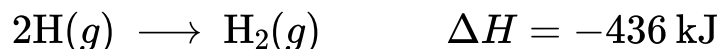
Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **pure covalent bond**. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:
Equation:

$$Cl + Cl \longrightarrow Cl_2$$
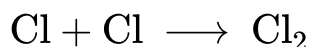
The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent bond**, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. [link] shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to [link], which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in [link].
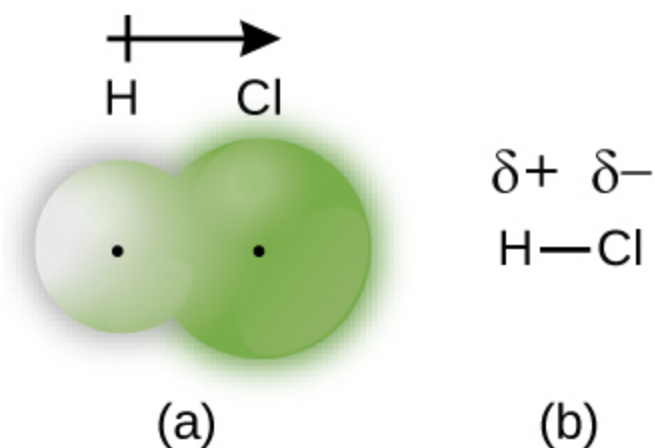
(a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols $\delta+$ and $\delta-$ indicate the polarity of the H–Cl bond.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

[link] shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling ([link]). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)
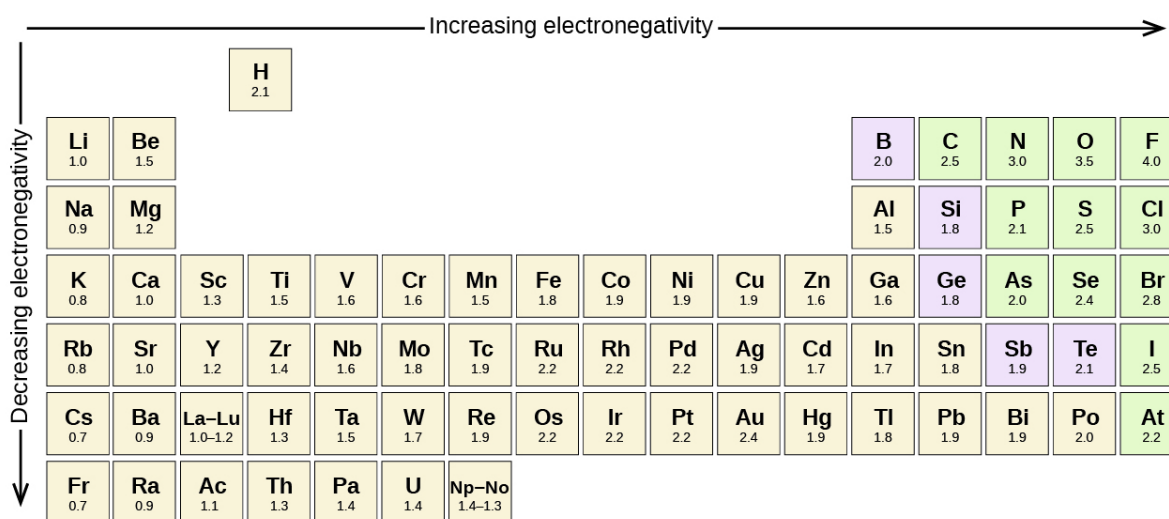
The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Note:
Linus Pauling
Linus Pauling, shown in [link], is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.
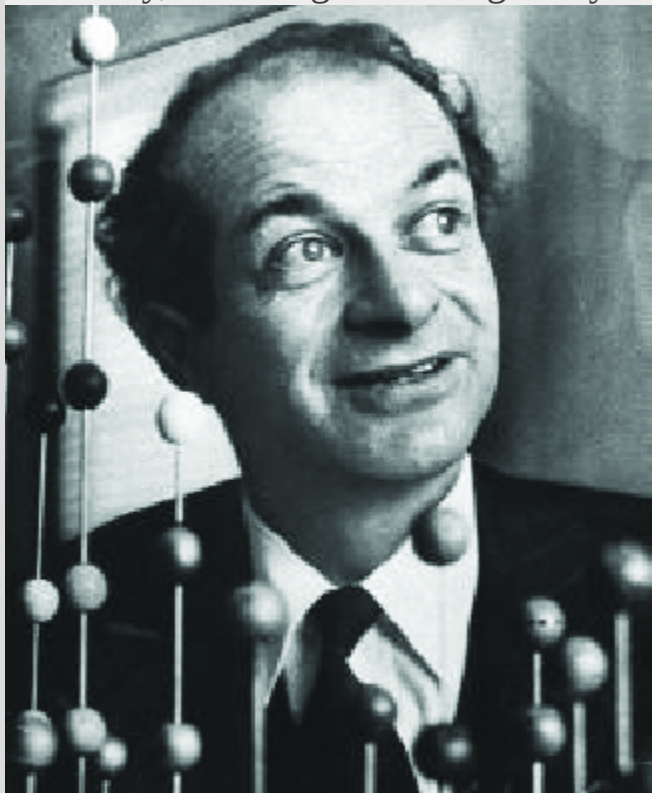
Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). [link] shows the relationship between electronegativity difference and bond type.

Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8
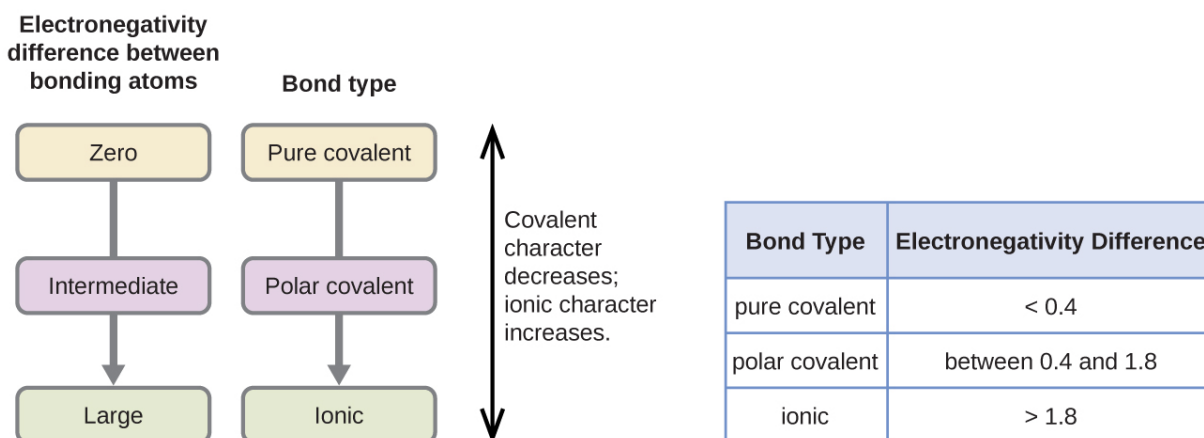
As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in [link]. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, NO_3^-, and NH_4^+, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic NO_3^- anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic

attraction between the ions K^+ and NO_3^-, as well as covalent between the nitrogen and oxygen atoms in NO_3^-.

Example:

Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in [link], arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. [link] shows these bonds in order of increasing polarity.

Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{C}-\overset{\delta+}{H}$
S–H	0.4	$\overset{\delta-}{S}-\overset{\delta+}{H}$
C–N	0.5	$\overset{\delta+}{C}-\overset{\delta-}{N}$
N–H	0.9	$\overset{\delta-}{N}-\overset{\delta+}{H}$

Bond Polarity and Electronegativity Difference		
Bond	**ΔEN**	**Polarity**
C–O	1.0	$\overset{\delta+}{C}-\overset{\delta-}{O}$
O–H	1.4	$\overset{\delta-}{O}-\overset{\delta+}{H}$

Check Your Learning

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in [link], arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Note:
Answer:

Bond	**Electronegativity Difference**	**Polarity**
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{C}-\overset{\delta+}{H}$
Si–C	0.7	$\overset{\delta+}{Si}-\overset{\delta-}{C}$

Bond	Electronegativity Difference	Polarity
Si–O	1.7	$\overset{\delta+}{Si} - \overset{\delta-}{O}$

Key Concepts and Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

Chemistry End of Chapter Exercises

Exercise:

Problem: Why is it incorrect to speak of a molecule of solid NaCl?

Solution:

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

Exercise:

Problem:

What information can you use to predict whether a bond between two atoms is covalent or ionic?

Exercise:

Problem:

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

(a) Cl_2CO

(b) MnO

(c) NCl_3

(d) $CoBr_2$

(e) K_2S

(f) CO

(g) CaF_2

(h) HI

(i) CaO

(j) IBr

(k) CO_2

Solution:

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

Exercise:

Problem:

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

Exercise:

Problem:

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) Br or Cl

(b) N or O

(c) S or O

(d) P or S

(e) Si or N

(f) Ba or P

(g) N or K

Solution:

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

Exercise:

Problem:

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) N or P

(b) N or Ge

(c) S or F

(d) Cl or S

(e) H or C

(f) Se or P

(g) C or Si

Exercise:

Problem:

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, H, N, O

(b) Br, Cl, F, H, I

(c) F, H, O, P, S

(d) Al, H, Na, O, P

(e) Ba, H, N, O, As

Solution:

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

Exercise:

Problem:

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) As, H, N, P, Sb

(b) Cl, H, P, S, Si

(c) Br, Cl, Ge, H, Sr

(d) Ca, H, K, N, Si

(e) Cl, Cs, Ge, H, Sr

Exercise:

Problem:

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

Solution:

N, O, F, and Cl

Exercise:

Problem: Which is the most polar bond?

(a) C–C

(b) C–H

(c) N–H

(d) O–H

(e) Se–H

Exercise:

Problem:

Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCl

(b) NO or CO

(c) SH or OH

(d) PCl or SCl

(e) CH or NH

(f) SO or PO

(g) CN or NN

Solution:

(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

Exercise:

Problem:

Which of the following molecules or ions contain polar bonds?

(a) O_3

(b) S_8

(c) O_2^{2-}

(d) NO_3^-

(e) CO_2

(f) H_2S

(g) BH_4^-

Glossary

bond length

distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond
bond formed when electrons are shared between atoms

electronegativity
tendency of an atom to attract electrons in a bond to itself

polar covalent bond
covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

pure covalent bond
(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

Lewis Symbols and Structures
By the end of this section, you will be able to:

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons:

$$\cdot Ca \cdot$$

[link] shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na ·
magnesium	$[Ne]3s^2$	· Mg ·
aluminum	$[Ne]3s^23p^1$	· Äl ·
silicon	$[Ne]3s^23p^2$	· Si ·
phosphorus	$[Ne]3s^23p^3$	· P ·
sulfur	$[Ne]3s^23p^4$	: S ·
chlorine	$[Ne]3s^23p^5$	: Cl ·
argon	$[Ne]3s^23p^6$	: Ar :

Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:

Na· ⟶ Na⁺ + e⁻   ·Ca· ⟶ Ca²⁺ + 2e⁻
sodium   sodium   calcium   calcium
atom   cation   atom   cation

Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:

:Cl· + e⁻ ⟶ :Cl:⁻   :S· + 2e⁻ ⟶ :S:²⁻
chlorine   chlorine   sulfur   sulfide
atom   anion   atom   anion

[link] demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal	Nonmetal	Ionic Compound
Na · sodium atom	+ :Cl· chlorine atom	⟶ Na⁺[:Cl:]⁻ sodium chloride (sodium ion and chloride ion)
·Mg· magnesium atom	+ :O· oxygen atom	⟶ Mg²⁺[:O:]²⁻ magnesium oxide (magnesium ion and oxide ion)
·Ca· calcium atom	+ 2:F· fluorine atoms	⟶ Ca²⁺[:F:]⁻₂ calcium fluoride (calcium ion and two fluoride ions)

Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:

chlorine
atoms

chlorine
molecule
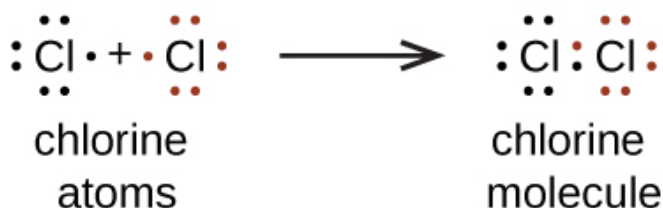
The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons

to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:
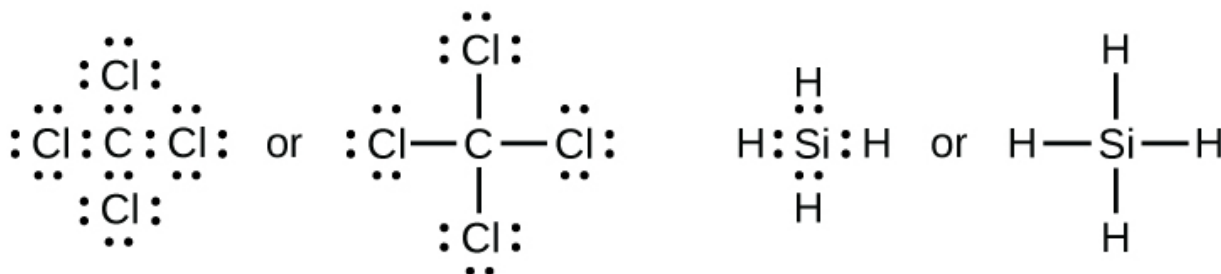
carbon tetrachloride

silane

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:
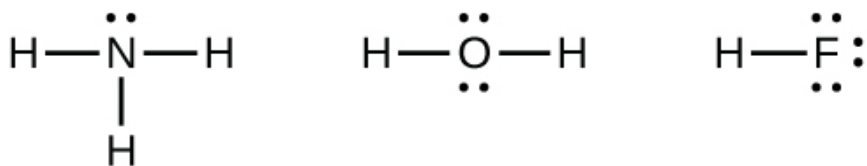
ammonia

Water

hydrogen fluoride

Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

formaldehyde

ethylene
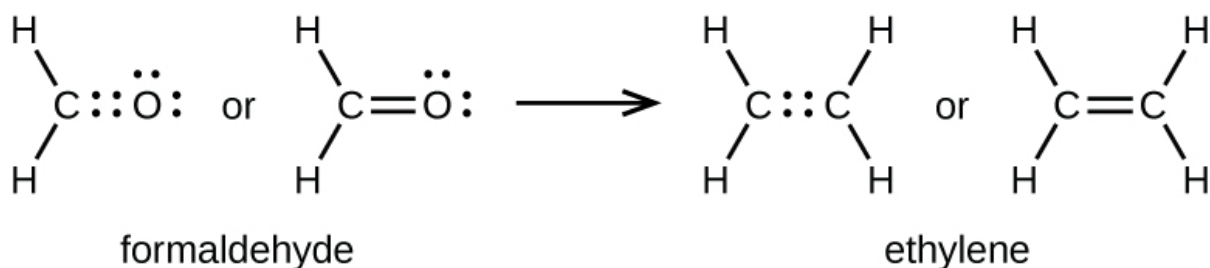
A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):

carbon monoxide

cyanide ion
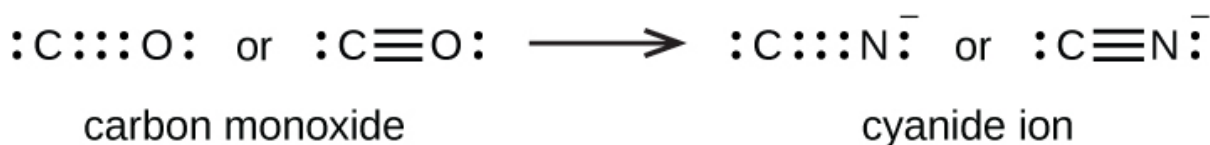
Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:
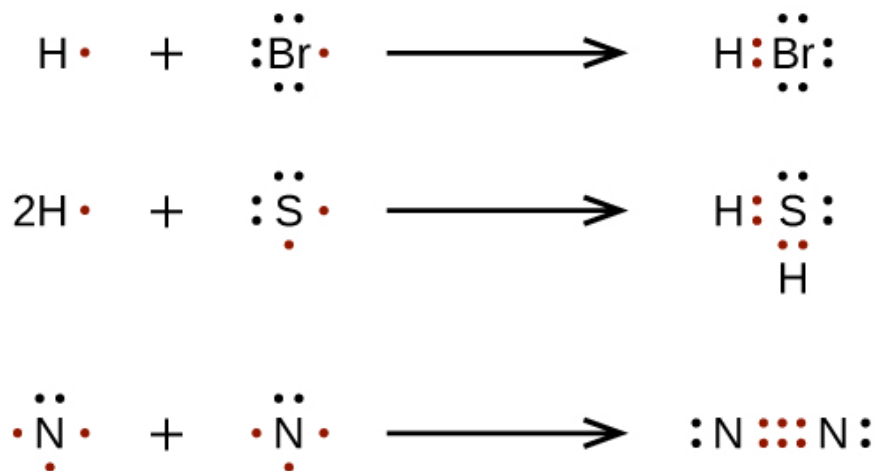
For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the

center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, $CHO_2{}^-$, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

  - For a molecule, we add the number of valence electrons on each atom in the molecule:
    Equation:

    SiH_4
    Si: 4 valence electrons/atom $\times$ 1 atom $= 4$
    $+$ H: 1 valence electron/atom $\times$ 4 atoms $= 4$

    $= 8$ valence electrons

  - For a *negative ion*, such as $CHO_2{}^-$, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):
    Equation:

    $CHO_2{}^-$
    C: 4 valence electrons/atom $\times$ 1 atom $= 4$
    H: 1 valence electron/atom $\times$ 1 atom $= 1$
    O: 6 valence electrons/atom $\times$ 2 atoms $= 12$
    $+$ $\qquad$ 1 additional electron $= 1$

    $= 18$ valence electrons

- For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:
  Equation:

  NO^+

  N: 5 valence electrons/atom $\times$ 1 atom = 5

  O: 6 valence electron/atom $\times$ 1 atom = 6
  $+ \; -1$ electron (positive charge) $= -1$

  $= 10$ valence electrons

- Since OF_2 is a neutral molecule, we simply add the number of valence electrons:
  Equation:

  OF_2

  O: 6 valence electrons/atom $\times$ 1 atom = 6
  $+$ F: 7 valence electrons/atom $\times$ 2 atoms = 14

  $= 20$ valence electrons

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)
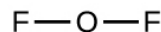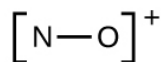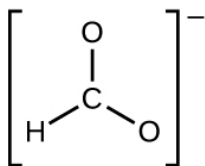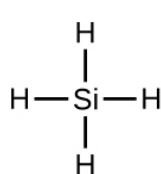
When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less

electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

   o There are no remaining electrons on SiH_4, so it is unchanged:
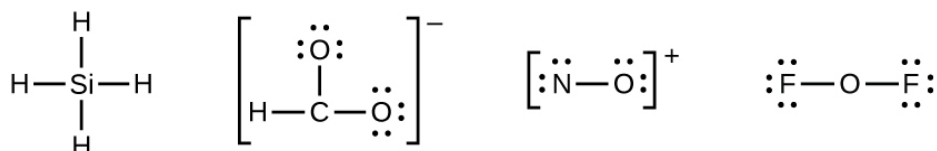
4. Place all remaining electrons on the central atom.

   o For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   o For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:
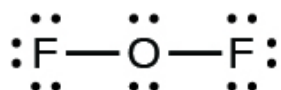
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

   o SiH_4: Si already has an octet, so nothing needs to be done.
   o CHO_2^- : We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:

gives
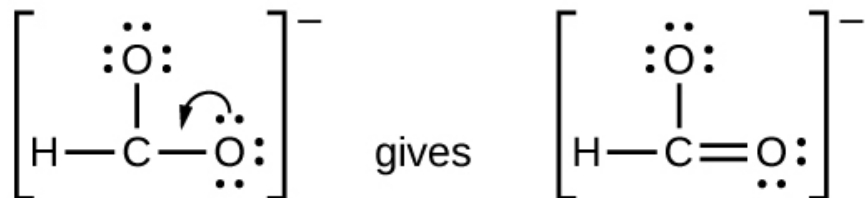
   o NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:

$$\left[:\overset{..}{N}\overset{\frown}{\longrightarrow}\overset{..}{O}:\right]^{+} \quad \text{gives} \quad \left[:\overset{..}{N}=\overset{..}{O}:\right]^{+}$$
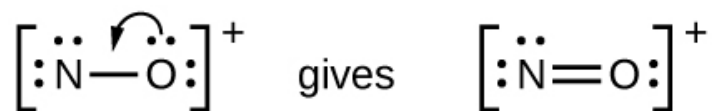
This still does not produce an octet, so we must move another pair, forming a triple bond:

$$\left[:N\equiv O:\right]^{+}$$
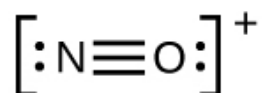
- In OF_2, each atom has an octet as drawn, so nothing changes.

Example:
Writing Lewis Structures
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?
Solution

Calculate the number of valence electrons.	HCN: $(1 \times 1) + (4 \times 1) + (5 \times 1) = 10$	H_3CCH_3: $(3 \times 1) + (4 \times 4) + (5 \times 1) = 14$	HCCH: $(1 \times 1) + (4 \times 4) + (1 \times 1) = 10$	NH_3: $(5 \times 1) + (3 \times 1) = 8$
Draw a skeleton and connect the atoms with single bonds.	Remember that H is never a central atom:			

Where needed, distribute electrons to the terminal atoms:			
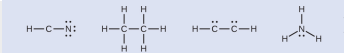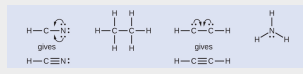
Where needed, distribute electrons to the terminal atoms:	HCN: six electrons placed on N	H_3CCH_3: no electrons remain	HCCH: no terminal atoms capable of accepting electrons	NH_3: no terminal atoms capable of accepting electrons
Where	HCN:	H_3CCH_3: no	HCCH:	NH_3: two

needed, place remaining electrons on the central atom:	H—C—N̈: H—C—C—H (with H's) H—C̈—C̈—H H—N̈—H (with H)		no electrons remain		four electrons remain	electrons placed on carbon	electrons placed on nitrogen
Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:	HCN: form two more C–N bonds	H₃CCH₃: all atoms have the correct number of electrons	HCCH: form a triple bond between the two carbon atoms	NH₃: all atoms have the correct number of electrons	H—C—N̈: gives H—C≡N: H—C—C—H gives H—C̈—C̈—H gives H—C≡C—H H—N̈—H		

Check Your Learning

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Note:
Answer:

:C≡O: :Ö=C=Ö:

Note:

Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley ([link]), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule ([link]). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This

type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.
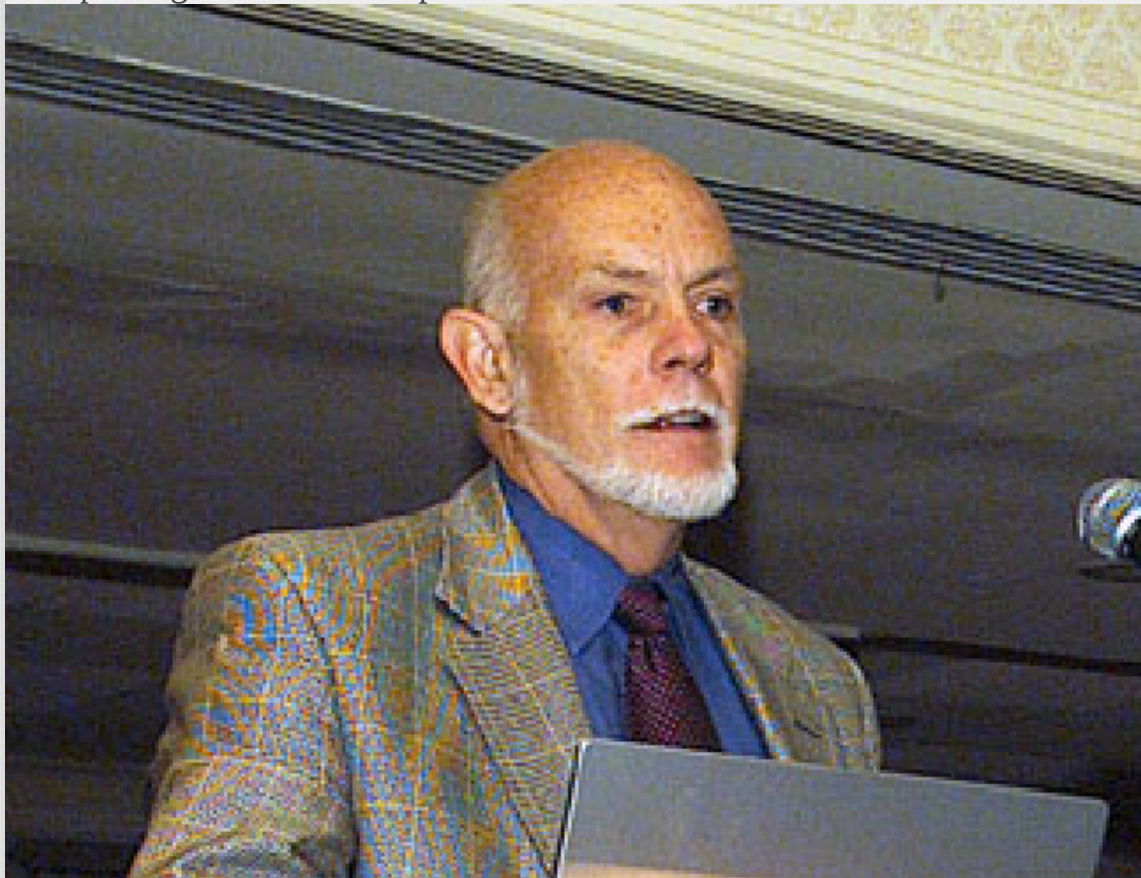
Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons.* The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule.* We can easily draw a skeleton with an N–O single bond:
   N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms.* In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:
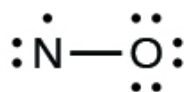
4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

$$:N=O:$$
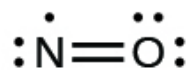
Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 12, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.

$$H-Be-H$$
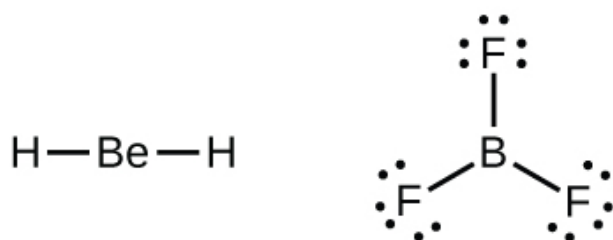
An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:
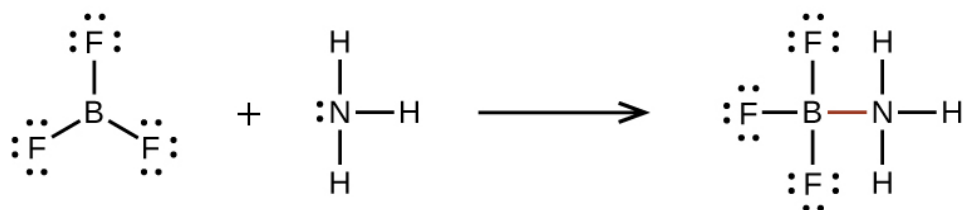
Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one $2s$ and three $2p$ orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty d orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules**. [link] shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.
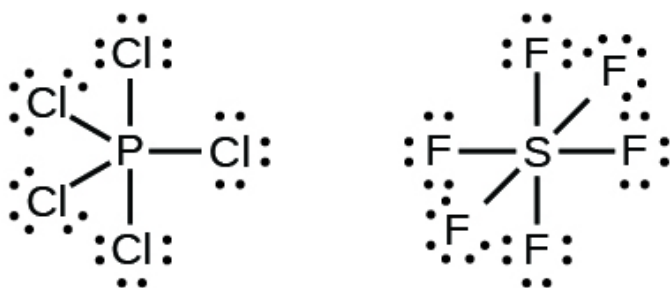
In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:
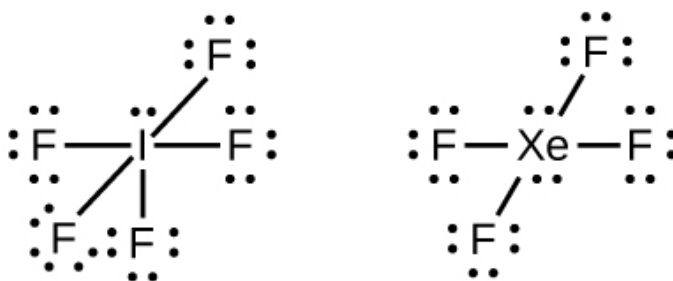
When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example:

Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

		XeF2: $8 + (2 \times 7) = 22$	XeF6: $8 + (6 \times 7) = 50$
Calculate the number of valence electrons:			
Draw a skeleton joining the atoms by single bonds.	Xenon will be the central atom because fluorine cannot be a central atom:	F—Xe—F	
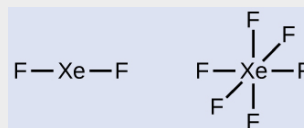
Distribute the remaining electrons.	XeF2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell	*d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF	2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:	XeF6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:

Check Your Learning

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and $ICl_4{}^-$.

Note:
Answer:
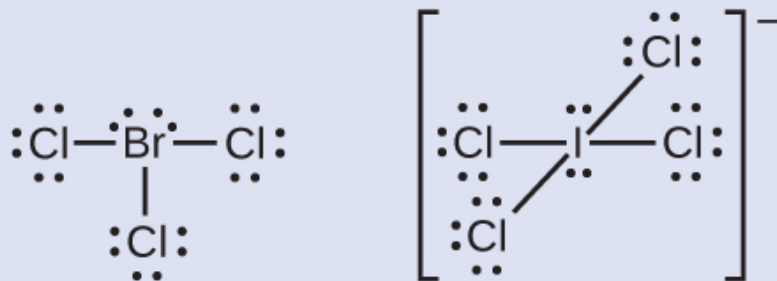
Key Concepts and Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Chemistry End of Chapter Exercises

Exercise:

Problem: Write the Lewis symbols for each of the following ions:

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) O^{2-}

(e) Ga^{3+}

(f) Li^+

(g) N^{3-}

Solution:

(a) eight electrons:

$$:\overset{\displaystyle ..}{\underset{\displaystyle ..}{As}}:^{3-}$$

;
(b) eight electrons:

$$\overset{\displaystyle ..}{:\underset{\displaystyle ..}{I}:}^{-}$$
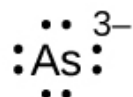
;
(c) no electrons
Be^{2+};
(d) eight electrons:

$$:\overset{\displaystyle ..}{\underset{\displaystyle ..}{O}}:^{2-}$$
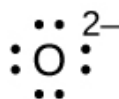
;
(e) no electrons
Ga^{3+};
(f) no electrons
Li^{+};
(g) eight electrons:

$$:\overset{\displaystyle ..}{\underset{\displaystyle ..}{N}}:^{3-}$$
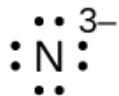
Exercise:

Problem:

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

Exercise:

Problem:

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b) Al_2O_3

(c) $GaCl_3$

(d) K_2O

(e) Li_3N

(f) KF

Solution:

(a)

Mg^{2+} $:\overset{\displaystyle ..}{\underset{\displaystyle ..}{S}}:^{2-}$

;
(b)

Al^{3+} $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{2-}$

;
(c)

Ga^{3+} $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^{-}$

;
(d)

K^{+} $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:^{2-}$

;
(e)

Li^{+} $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:^{3-}$

;
(f)

K^{+} $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:^{-}$
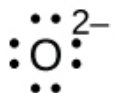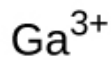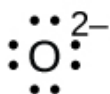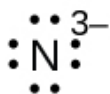
Exercise:

Problem:

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

(a)

$$\left[M^{2+}\right]\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:\right]^{2-}$$

(b)

$$\left[M^{3+} \right]\left[:\ddot{\underset{..}{X}}: \right]_3^-$$

(c)

$$\left[M^+ \right]_2\left[:\ddot{\underset{..}{X}}: \right]^{2-}$$

(d)

$$\left[M^{3+} \right]_2\left[:\ddot{\underset{..}{X}}: \right]_3^{2-}$$
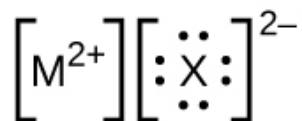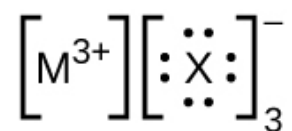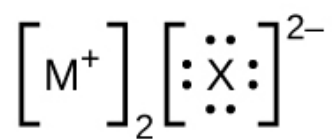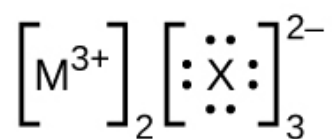
Exercise:

Problem:

Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

Solution:

$$:P\equiv P:$$

Exercise:

Problem: Write Lewis structures for the following:

(a) H_2

(b) HBr

(c) PCl_3

(d) SF_2

(e) H_2CCH_2

(f) $HNNH$

(g) H_2CNH

(h) NO^-

(i) N_2

(j) CO

(k) CN^-

Exercise:

Problem: Write Lewis structures for the following:

(a) O_2

(b) H_2CO

(c) AsF_3

(d) $ClNO$

(e) $SiCl_4$

(f) H_3O^+

(g) $NH_4{}^+$

(h) $BF_4{}^-$

(i) $HCCH$

(j) $ClCN$

(k) $C_2{}^{2+}$

Solution:

(a)

$$\ddot{O}=\ddot{O}:$$
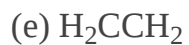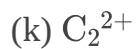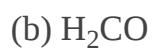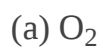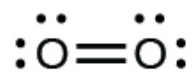
In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

(b)
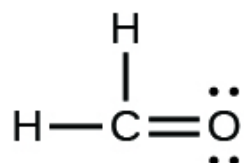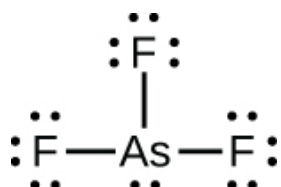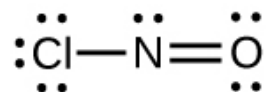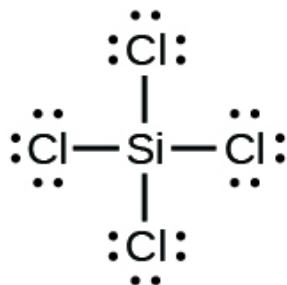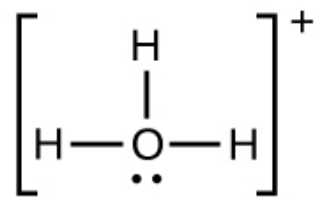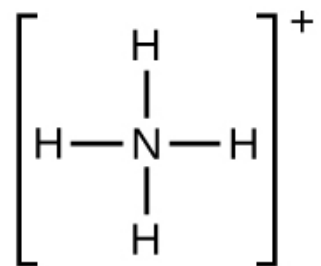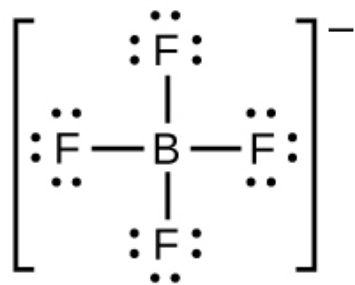
$$H-\overset{\overset{\displaystyle H}{|}}{C}=\ddot{O}$$

;

(c)

$$:\ddot{F}-\overset{\overset{\displaystyle :\ddot{F}:}{|}}{As}-\ddot{F}:$$

;

(d)

$$:\ddot{Cl}-\ddot{N}=\ddot{O}$$

;

(e)

$$:\ddot{Cl}-\overset{\overset{\displaystyle :\ddot{Cl}:}{|}}{\underset{\underset{\displaystyle :\ddot{Cl}:}{|}}{Si}}-\ddot{Cl}:$$

;

(f)

;
(g)

;
(h)

;
(i)

;
(j)

;
(k)

$$C\equiv C^{2+}$$

Exercise:

Problem: Write Lewis structures for the following:

(a) SeF_6

(b) XeF_4

(c) $SeCl_3^+$

(d) Cl_2BBCl_2 (contains a B–B bond)

Solution:

(a) SeF_6:

;

(b) XeF_4:

;

(c) $SeCl_3^+$:

;
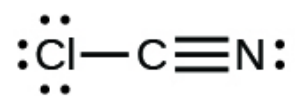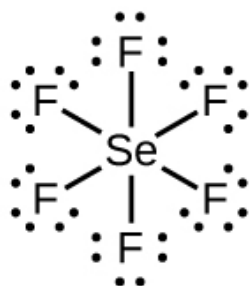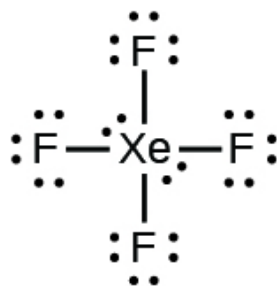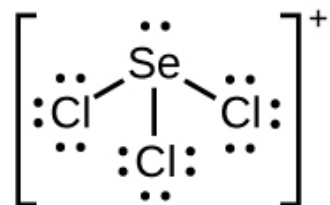
(d) Cl_2BBCl_2:
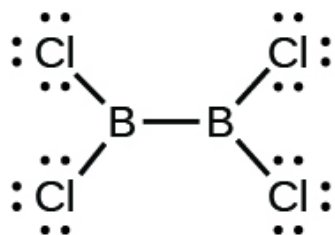
Exercise:

Problem: Write Lewis structures for:

(a) $PO_4{}^{3-}$

(b) $ICl_4{}^-$

(c) $SO_3{}^{2-}$

(d) HONO

Exercise:

Problem:

Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

Solution:

$$2\ CH_3OH + 3\ O_2 \longrightarrow 2\ CO_2 + 4\ H_2O$$

$$CH_3CH_2OH + 3\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$$
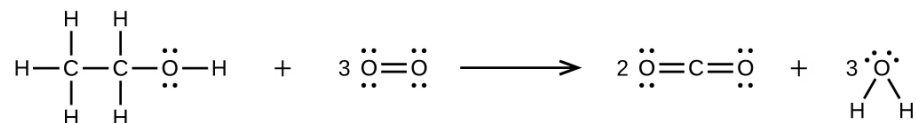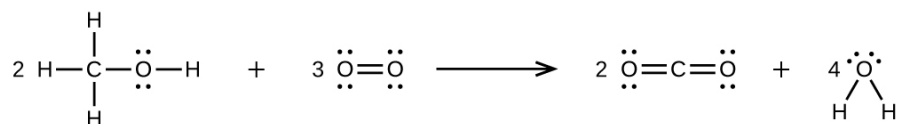
Exercise:

Problem:

Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

Exercise:

Problem:

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

Solution:
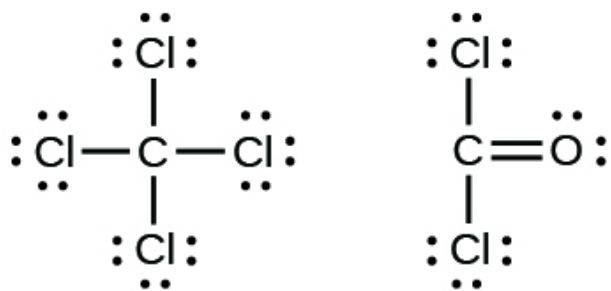
Exercise:

Problem:

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

(a) the amino acid serine:

```
        O—H
        |
    H—C—H
    |       O
    |       |
H—N—C—C—O—H
    |
    H
```

(b) urea:

```
  H   O   H
  |   |   |
H—N—C—N—H
```

(c) pyruvic acid:

```
  H   O   O
  |   |   |
H—C—C—C—O—H
  |
  H
```
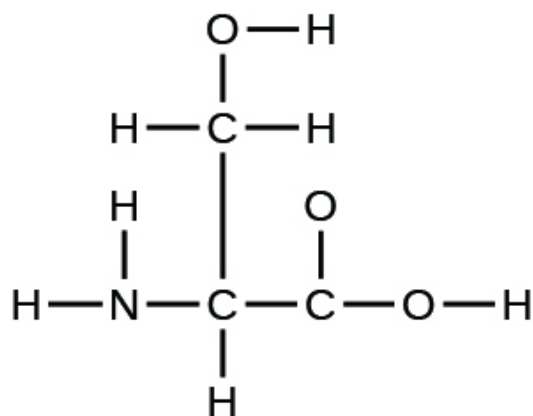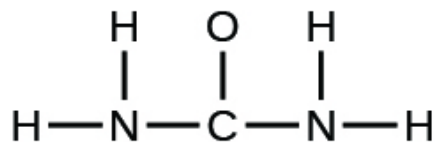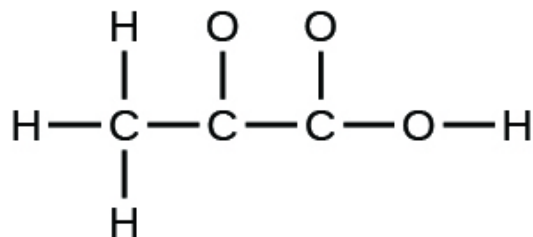
(d) uracil:
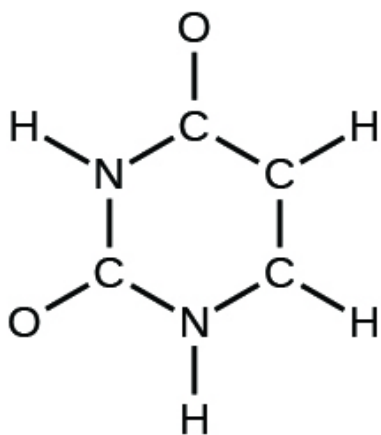
(e) carbonic acid:
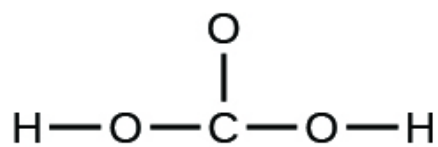
Solution:

(a)
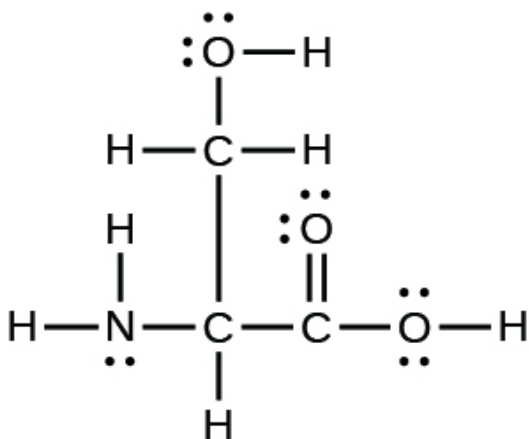
;
(b)
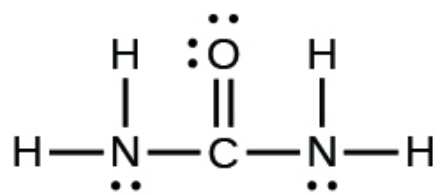
;
(c)

;
(d)

;
(e)
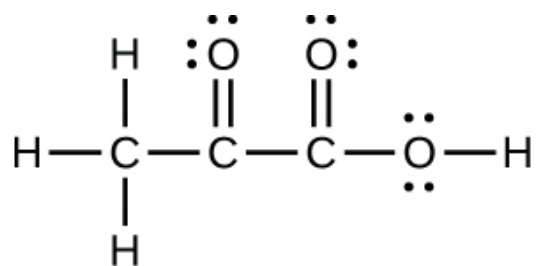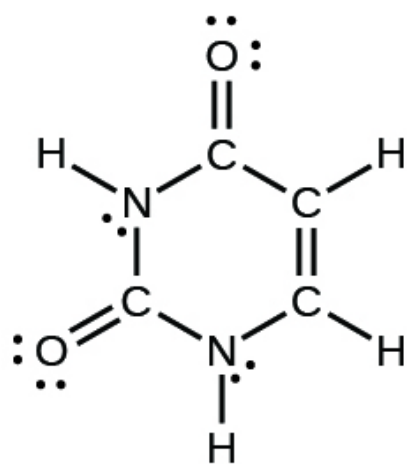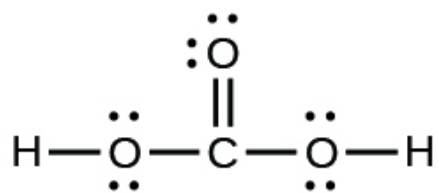
Exercise:

Problem: How are single, double, and triple bonds similar? How do they differ?

Solution:

Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

Glossary

double bond
    covalent bond in which two pairs of electrons are shared between two atoms

free radical
    molecule that contains an odd number of electrons

hypervalent molecule
    molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure
    diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol
    symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair
    two (a pair of) valence electrons that are not used to form a covalent bond

octet rule
    guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond
    bond in which a single pair of electrons is shared between two atoms

triple bond
    bond in which three pairs of electrons are shared between two atoms

Molecular Structure and Polarity
By the end of this section, you will be able to:

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space ([link]). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).
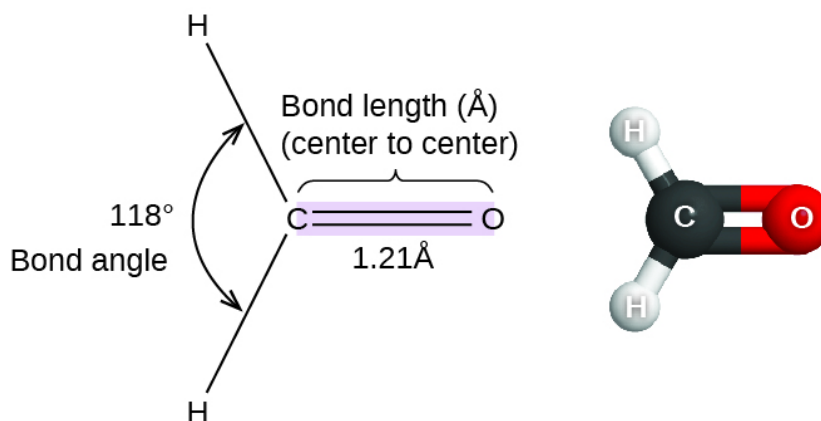
Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that

electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.
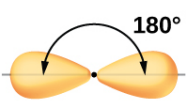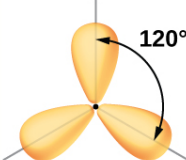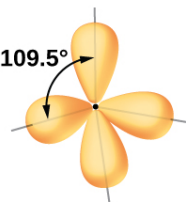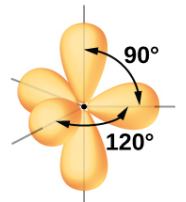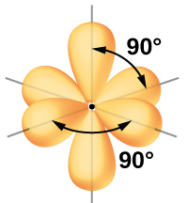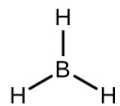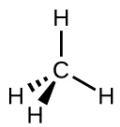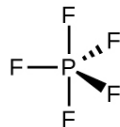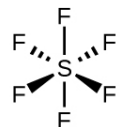
As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 ([link]) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° ([link]).
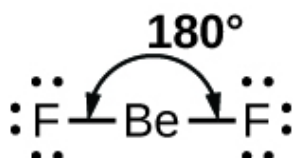
The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

[link] illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a

linear geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.

|	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Number of regions					
Spatial arrangement	180°	120°	109.5°	90° 120°	90° 90°
Line-dash-wedge notation	H—Be—H	H, B, H, H	H, C, H, H, H	F, P, F, F, F, F	F, S, F, F, F, F
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in [link] describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure ([link]). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule ([link]).
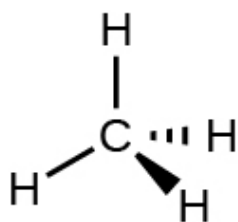
The molecular structure of the methane molecule, CH_4, is shown with

a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.
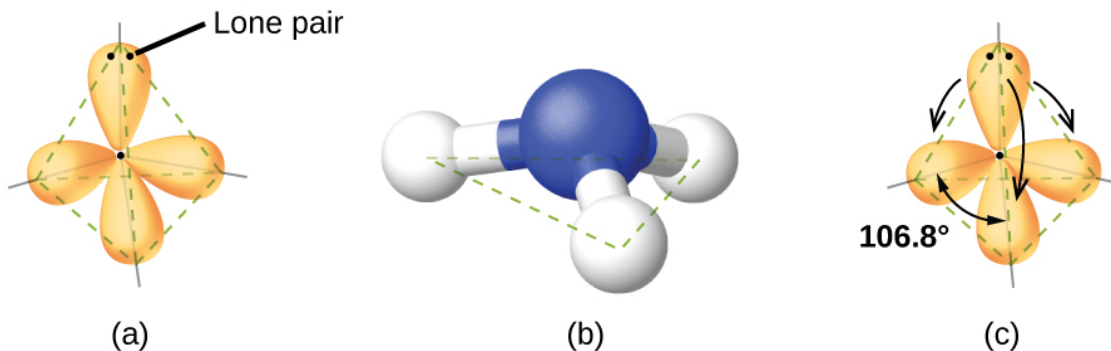
(a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in [link], small distortions from the ideal angles in [link] can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

Equation:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:
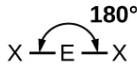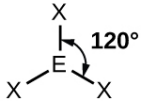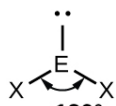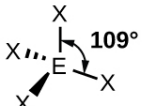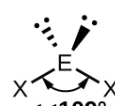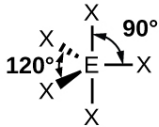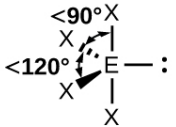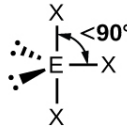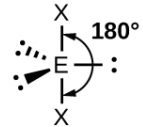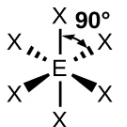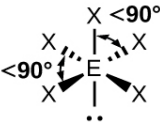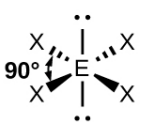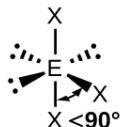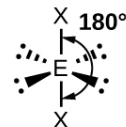
Equation:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens ([link]). This molecule has regions of high electron

density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid ([link]) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron ([link]) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion ([link]). [link] illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	**180°** X—E—X Linear				
3	X **120°** X—E—X Trigonal planar	X—E—X **<120°** Bent or angular			
4	X **109°** X—E—X Tetrahedral	X—E—X **<109°** Trigonal pyramid	X—E—X **<<109°** Bent or angular		
5	X **90°** **120°** X—E—X X Trigonal bipyramid	**<90°** X **<120°** X—E—: X Sawhorse or seesaw	X **<90°** X—E—X X T-shape	X **180°** X—E—: X Linear	
6	X **90°** X—E—X X Octahedral	X **<90°** X—E—X X Square pyramid	X **90°** X—E—X X Square planar	X X—E—X X **<90°** T-shape	X **180°** X—E—X X Linear

The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in [link]) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in [link]: an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis

around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in [link], the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule ([link]). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.
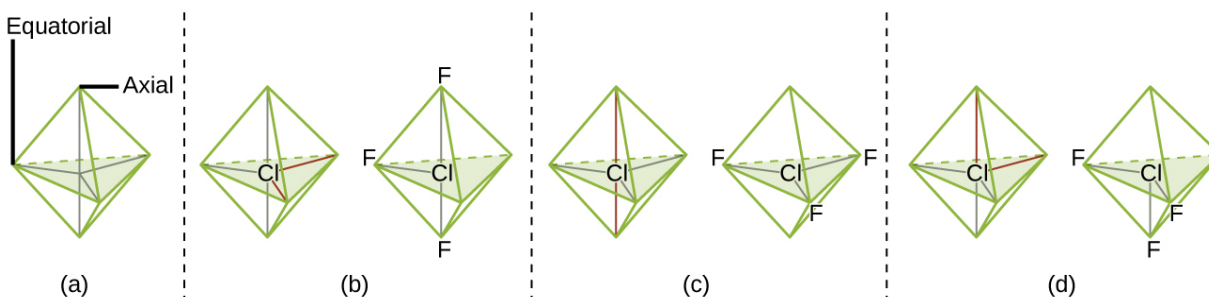
(a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions ([link]).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral ([link], first column).
4. Use the number of lone pairs to determine the molecular structure ([link]). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.
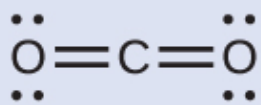
Example:
Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3
Predict the electron-pair geometry and molecular structure for each of the following:
(a) carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
(b) boron trichloride, BCl_3, an important industrial chemical
Solution
(a) We write the Lewis structure of CO_2 as:

This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:
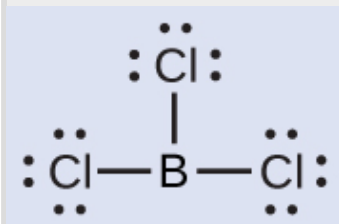
Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure ([link]).
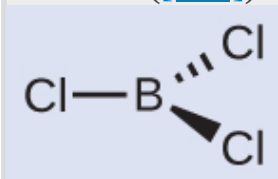
The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Check Your Learning

Carbonate, $CO_3{}^{2-}$, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Note:
Answer:
The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Example:

Predicting Electron-pair Geometry and Molecular Structure: Ammonium
Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.
Solution
We write the Lewis structure of NH_4^+ as:
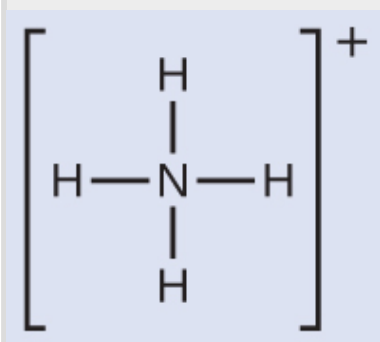
We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle ([link]). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral ([link]).
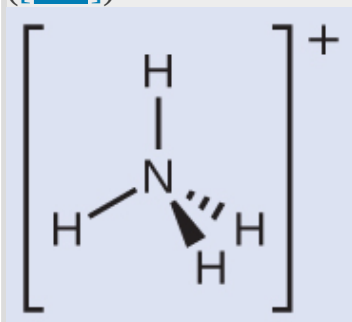
The ammonium ion displays a tetrahedral

electron-pair
geometry as well
as a tetrahedral
molecular
structure.

Check Your Learning

Identify a molecule with trigonal bipyramidal molecular structure.

Note:
Answer:

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example:
Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:
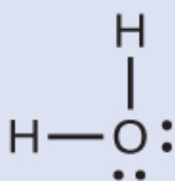
We predict that these four regions are arranged in a tetrahedral fashion ([link]), as indicated in [link]. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.
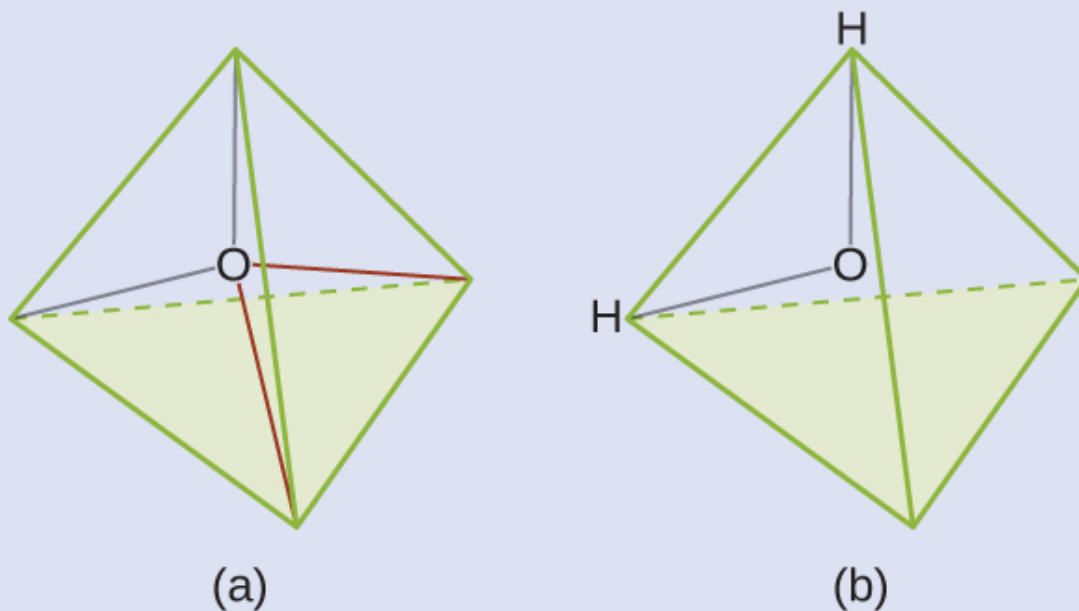
(a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Check Your Learning
The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Note:
Answer:
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Molecular Structure for Multicenter Molecules

When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

Example:
Predicting Structure in Multicenter Molecules
The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:
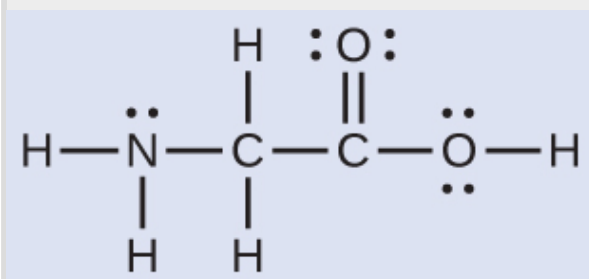
Solution
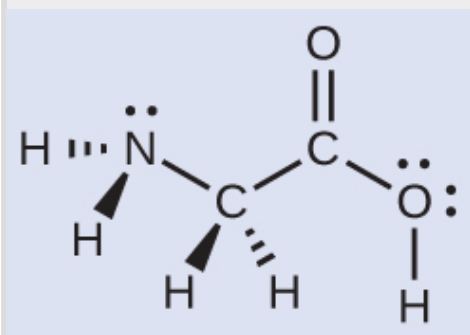
Consider each central atom independently. The electron-pair geometries:

- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral

- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

Check Your Learning
Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:
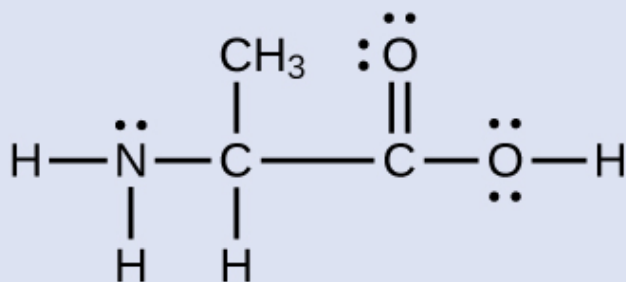
Note:
Answer:
electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

Note:

The [molecular shape simulator](#) lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example:
Molecular Simulation
Using [molecular shape simulator](#) allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under "Options" on the right. We can also use the "Name" checkboxes at bottom-left to display or hide the electron pair geometry (called "electron geometry" in the simulator) and/or molecular structure (called "molecular shape" in the simulator).
Build the molecule HCN in the simulator based on the following Lewis structure:
Equation:

$$H–C \equiv N$$
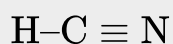
Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?
Solution
The molecular structure is linear.
Check Your Learning
Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Note:
Answer:

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge ($\delta+$) and the other atom with a partial negative charge ($\delta-$), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ).

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude ([link]). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.
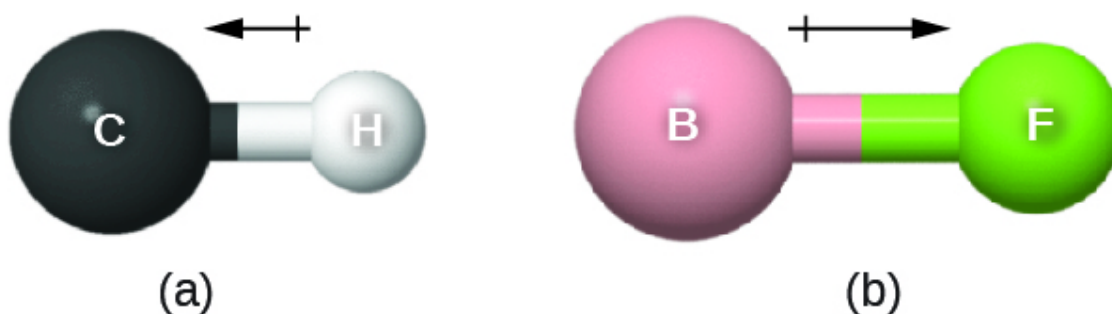
(a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 ([link]). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule ([link]), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

Bond moments

Bond moments

Overall dipole moment = 0
(a)

Overall dipole moment
(b)
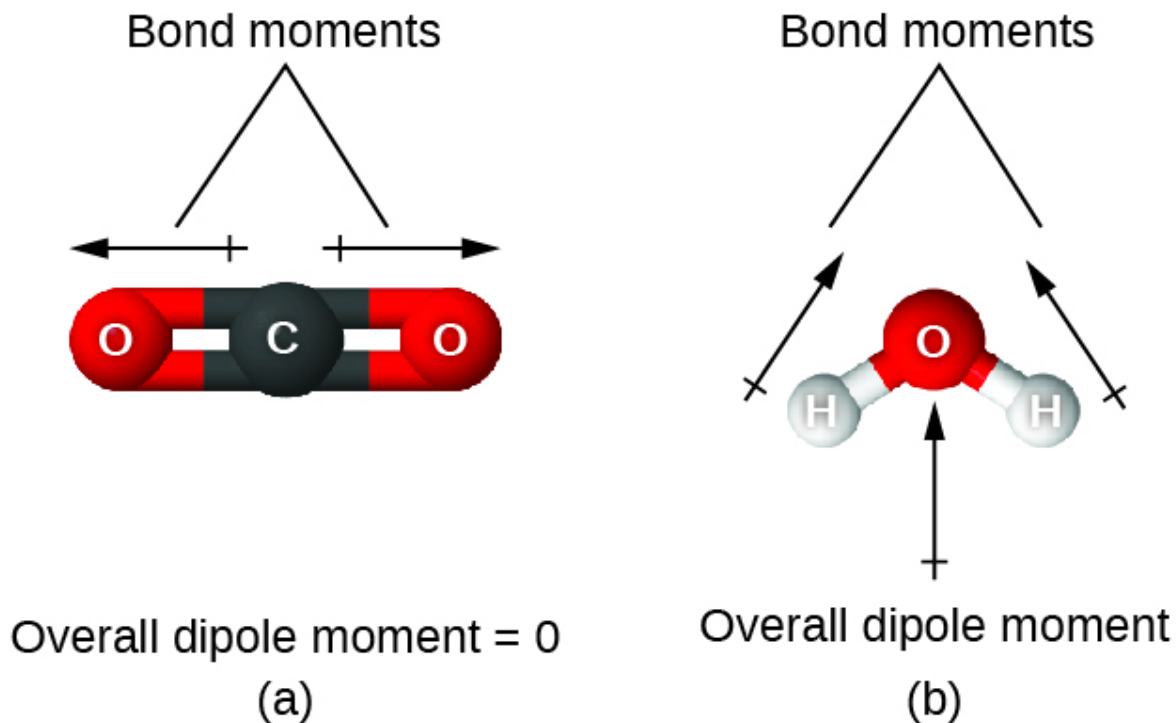
The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

Bond moments

Overall dipole moment
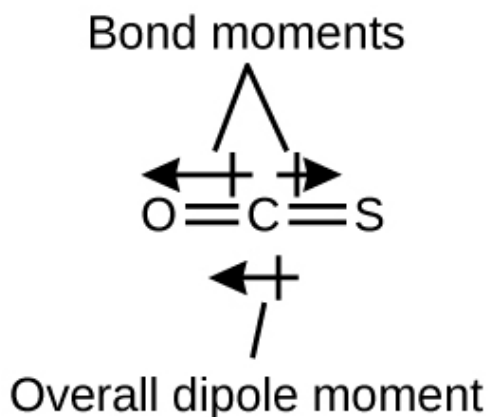
The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is another example of a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other. All of the dipoles have a downward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:
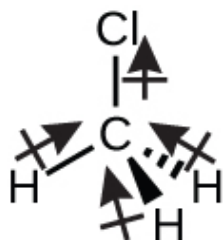
When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3. A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:
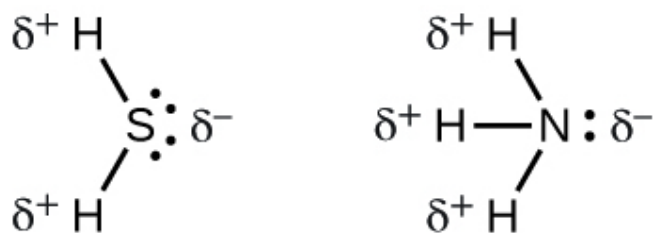
To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate ([link]). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.
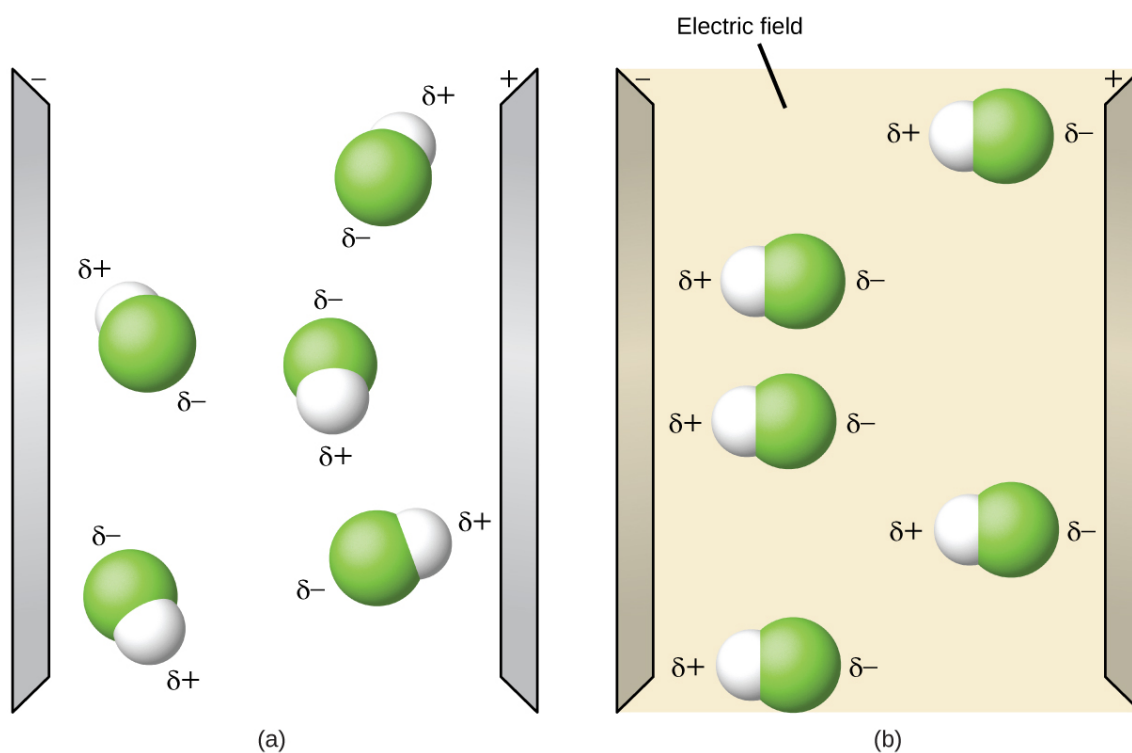
(a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Note:

The molecule polarity simulation provides many ways to explore dipole moments of bonds and molecules.

Key Concepts and Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in

a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

Solution:

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

Exercise:

Problem:

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

Exercise:

Problem:

Explain the difference between electron-pair geometry and molecular structure.

Solution:

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

Exercise:

Problem:

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?

Exercise:

Problem:

Explain how a molecule that contains polar bonds can be nonpolar.

Solution:

As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

Exercise:

Problem:

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

Exercise:

Problem:

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) SF_6

(b) PCl_5

(c) BeH_2

(d) $CH_3{}^+$

Solution:

(a) Both the electron geometry and the molecular structure are octahedral.
(b) Both the electron geometry and the molecular structure are trigonal bipyramid.
(c) Both the electron geometry and the molecular structure are linear.
(d) Both the electron geometry and the molecular structure are trigonal planar.

Exercise:

Problem:

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

(a) ClF_5

(b) $ClO_2{}^-$

(c) $TeCl_4{}^{2-}$

(d) PCl_3

(e) SeF_4

(f) $PH_2{}^-$

Solution:

(a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

Exercise:

Problem:

Identify the electron pair geometry and the molecular structure of each of the following molecules:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

Solution:

(a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

Exercise:

Problem:

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4{}^{2-}$

(d) PCl_3

(e) SeF_4

(f) $PH_2{}^-$

(g) XeF_2

Solution:

All of these molecules and ions contain polar bonds. Only ClF_5, $ClO_2{}^-$, PCl_3, SeF_4, and $PH_2{}^-$ have dipole moments.

Exercise:

Problem: Which of the following molecules have dipole moments?

(a) CS_2

(b) SeS_2

(c) CCl_2F_2

(d) PCl_3 (P is the central atom)

(e) $ClNO$ (N is the central atom)

Solution:

SeS_2, CCl_2F_2, PCl_3, and $ClNO$ all have dipole moments.

Exercise:

Problem:

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

Solution:

P

Exercise:

Problem:

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

Exercise:

Problem:

Draw the Lewis structures and predict the shape of each compound or ion:

(a) CO_2

(b) NO_2^-

(c) SO_3

(d) SO_3^{2-}

Exercise:

Problem:

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

Solution:

B—A—B CO_2, linear
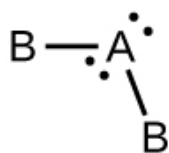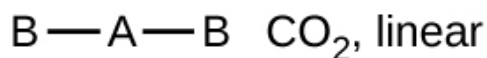
B—A H_2O, bent with an approximately 109° angle
  |
  B
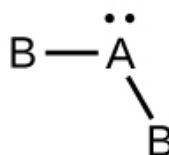
B—A SO_2, bent with an approximately 120° angle
  |
  B

Exercise:

Problem:

Use the simulation to perform the following exercises for a two-atom molecule:

(a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.

(b) With a partial positive charge on A, turn on the electric field and describe what happens.

(c) With a small partial negative charge on A, turn on the electric field and describe what happens.

(d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

Exercise:

Problem:

Use the simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

(a) Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.

(b) Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

Solution:

The molecular dipole points away from the hydrogen atoms.

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

Exercise:

Problem:

Use the [Molecule Shape simulator](#) to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the "real" and "model" modes. Explain the difference observed.

Solution:

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the "real" mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

Glossary

axial position

location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle
angle between any two covalent bonds that share a common atom

bond distance
(also, bond length) distance between the nuclei of two bonded atoms

bond dipole moment
separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

dipole moment
property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

electron-pair geometry
arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

equatorial position
one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

linear
shape in which two outside groups are placed on opposite sides of a central atom

molecular structure
structure that includes only the placement of the atoms in the molecule

octahedral
shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule
    (also, dipole) molecule with an overall dipole moment

tetrahedral
    shape in which four outside groups are placed around a central atom such
    that a three-dimensional shape is generated with four corners and 109.5°
    angles between each pair and the central atom

trigonal bipyramidal
    shape in which five outside groups are placed around a central atom such
    that three form a flat triangle with 120° angles between each pair and the
    central atom, and the other two form the apex of two pyramids, one above
    and one below the triangular plane

trigonal planar
    shape in which three outside groups are placed in a flat triangle around a
    central atom with 120° angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)
    theory used to predict the bond angles in a molecule based on positioning
    regions of high electron density as far apart as possible to minimize
    electrostatic repulsion

vector
    quantity having magnitude and direction

Introduction

class="introduction"

- Gas Pressure
- Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- Effusion and Diffusion of Gases
- The Kinetic-Molecular Theory
- Non-Ideal Gas Behavior

The hot air inside these balloons is less dense than the surrounding cool air. This results in a buoyant force that causes the balloons to rise when their guy lines are untied. (credit: modification of work by Anthony Quintano)

We are surrounded by an ocean of gas—the atmosphere—and many of the properties of gases are familiar to us from our daily activities. Heated gases expand, which can make a hot air balloon rise ([link]) or cause a blowout in a bicycle tire left in the sun on a hot day.

Gases have played an important part in the development of chemistry. In the seventeenth and eighteenth centuries, many scientists investigated gas behavior, providing the first mathematical descriptions of the behavior of matter.

In this chapter, we will examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

Gas Pressure
By the end of this section, you will be able to:

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects ([link]). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.
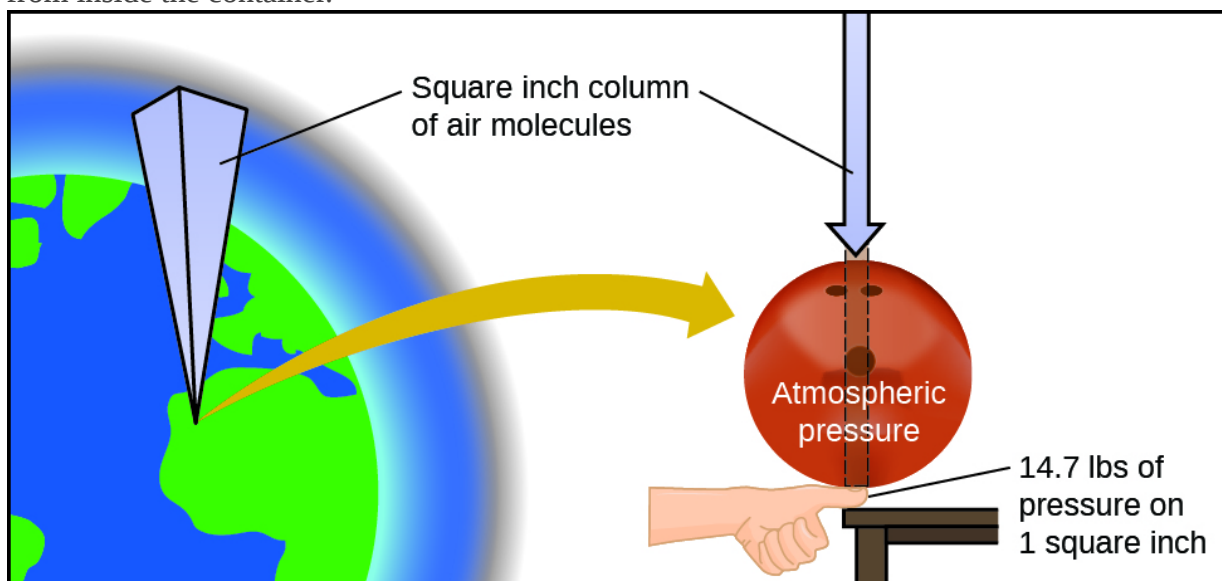
The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

Note:

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is *twice* the usual pressure, and the sensation is unpleasant.

In general, **pressure** is defined as the force exerted on a given area: $P = \frac{F}{A}$. Note that pressure is directly proportional to force and inversely proportional to area. Thus, pressure can be increased either by increasing the amount of force or by decreasing the area over which it is applied; pressure can be decreased by decreasing the force or increasing the area.

Let's apply this concept to determine which would be more likely to fall through thin ice in [link]—the elephant or the figure skater? A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:
Equation:

$$\text{pressure per elephant foot} = 14{,}000 \, \frac{\text{lb}}{\text{elephant}} \times \frac{1 \, \text{elephant}}{4 \, \text{feet}} \times \frac{1 \, \text{foot}}{250 \, \text{in}^2} = 14 \, \text{lb/in}^2$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:
Equation:

$$\text{pressure per skate blade} = 120 \, \frac{\text{lb}}{\text{skater}} \times \frac{1 \, \text{skater}}{2 \, \text{blades}} \times \frac{1 \, \text{blade}}{2 \, \text{in}^2} = 30 \, \text{lb/in}^2$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall though thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

Equation:

$$\text{pressure per human foot} = 120 \, \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2$$

(a)

(b)

Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi)

The SI unit of pressure is the **pascal (Pa)**, with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or **bar** (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—**pounds per square inch (psi)**—for example, in car tires. Pressure can also be measured using the unit **atmosphere (atm)**, which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). [link] provides some information on these and a few other common units for pressure measurements

Pressure Units	
Unit Name and Abbreviation	**Definition or Relation to Other Unit**

Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit
pascal (Pa)	1 Pa = 1 N/m^2 recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi
atmosphere (atm)	1 atm = 101,325 Pa air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly) commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa used by aviation industry, also some weather reports
torr	1 torr = $\frac{1}{760}$ atm named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr

Example:
Conversion of Pressure Units
The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:
(a) torr
(b) atm
(c) kPa
(d) mbar
Solution
This is a unit conversion problem. The relationships between the various pressure units are given in [link].
(a) $29.2 \ \cancel{\text{in Hg}} \ \times \ \frac{25.4 \ \cancel{\text{mm}}}{1 \ \cancel{\text{in}}} \ \times \ \frac{1 \ \text{torr}}{1 \ \cancel{\text{mm Hg}}} = 742 \ \text{torr}$
(b) $742 \ \cancel{\text{torr}} \ \times \ \frac{1 \ \text{atm}}{760 \ \cancel{\text{torr}}} = 0.976 \ \text{atm}$

(c) $742 \, \cancel{\text{torr}} \times \frac{101.325 \text{ kPa}}{760 \, \cancel{\text{torr}}} = 98.9 \text{ kPa}$

(d) $98.9 \, \cancel{\text{kPa}} \times \frac{1000 \, \cancel{\text{Pa}}}{1 \, \cancel{\text{kPa}}} \times \frac{1 \, \cancel{\text{bar}}}{100,000 \, \cancel{\text{Pa}}} \times \frac{1000 \text{ mbar}}{1 \, \cancel{\text{bar}}} = 989 \text{ mbar}$

Check Your Learning

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Note:
Answer:
0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a **barometer** ([link]). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.
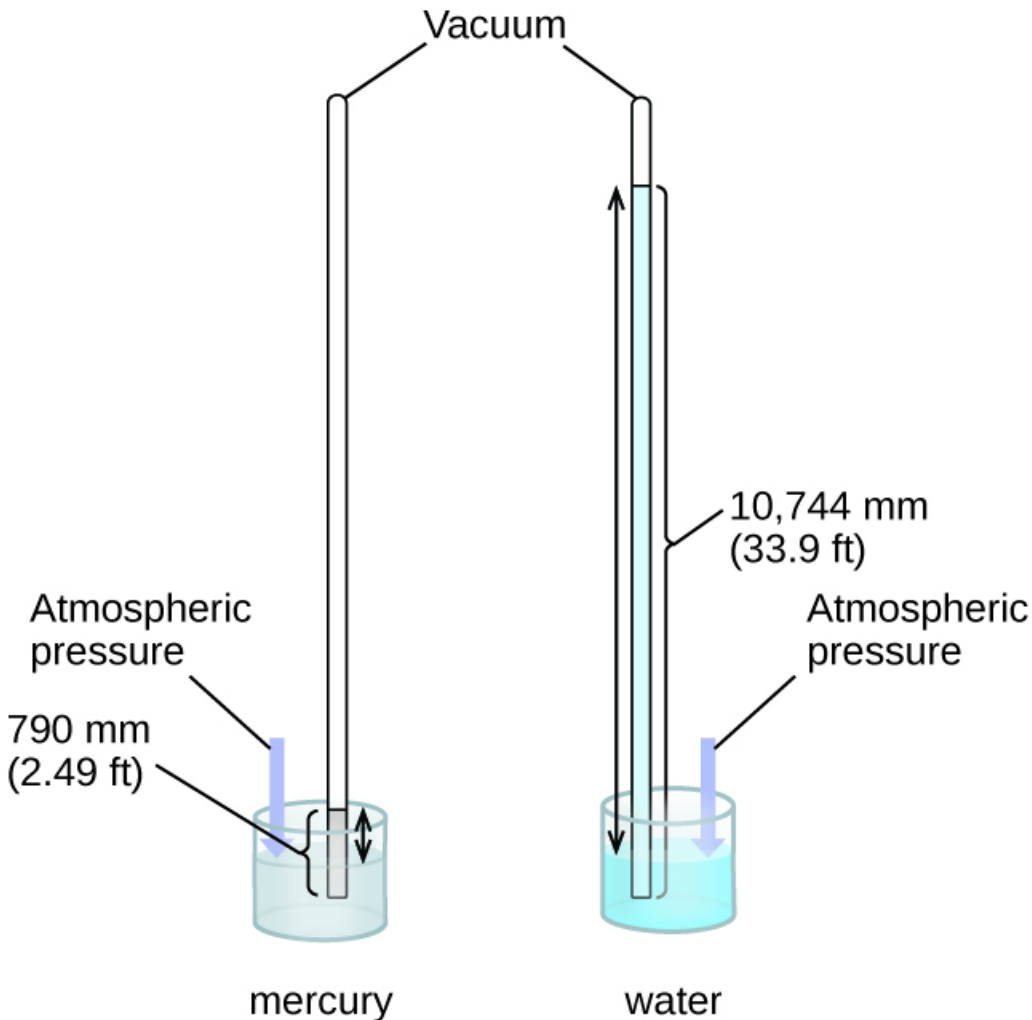
In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The **torr** was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as **hydrostatic pressure**, p:

Equation:

$$p = h\rho g$$

where h is the height of the fluid, ρ is the density of the fluid, and g is acceleration due to gravity.

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts ([link]) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.
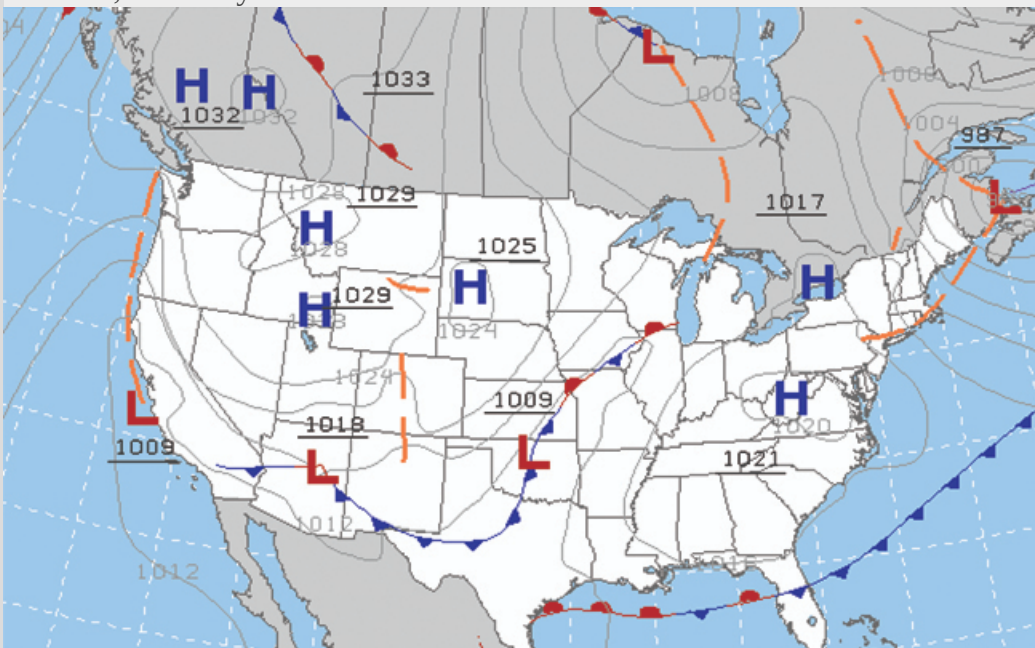
Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events. The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in [link]: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the

troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.
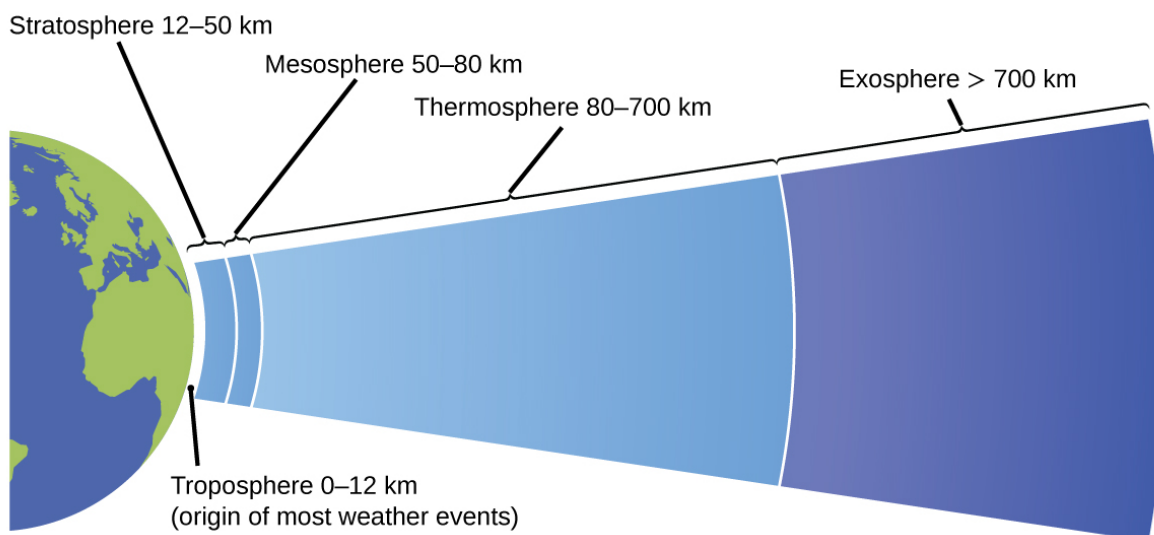
Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Key Concepts and Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Chemistry End of Chapter Exercises

Exercise:

Problem:

Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?

Solution:

The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

Exercise:

Problem:

Why do some small bridges have weight limits that depend on how many wheels or axles the crossing vehicle has?

Exercise:

Problem:

Why should you roll or belly-crawl rather than walk across a thinly-frozen pond?

Solution:

Lying down distributes your weight over a larger surface area, exerting less pressure on the ice compared to standing up. If you exert less pressure, you are less likely to break through thin ice.

Exercise:

Problem:

A typical barometric pressure in Redding, California, is about 750 mm Hg. Calculate this pressure in atm and kPa.

Exercise:

Problem:

A typical barometric pressure in Denver, Colorado, is 615 mm Hg. What is this pressure in atmospheres and kilopascals?

Solution:

0.809 atm; 82.0 kPa

Exercise:

Problem:

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, and in kilopascals?

Exercise:

Problem:

Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?

Solution:

2.2×10^2 kPa

Exercise:

Problem:

During the Viking landings on Mars, the atmospheric pressure was determined to be on the average about 6.50 millibars (1 bar = 0.987 atm). What is that pressure in torr and kPa?

Exercise:

Problem:

The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.

Solution:

Earth: 14.7 lb in^{-2}; Venus: 13.1×10^3 lb in^{-2}

Exercise:

Problem:

Consider this scenario and answer the following questions: On a mid-August day in the northeastern United States, the following information appeared in the local newspaper: atmospheric pressure at sea level 29.97 in., 1013.9 mbar.

(a) What was the pressure in kPa?

(b) The pressure near the seacoast in the northeastern United States is usually reported near 30.0 in. Hg. During a hurricane, the pressure may fall to near 28.0 in. Hg. Calculate the drop in pressure in torr.

Solution:

(a) 101.5 kPa; (b) 51 torr drop

Glossary

atmosphere (atm)
  unit of pressure; 1 atm = 101,325 Pa

bar
  (bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer
  device used to measure atmospheric pressure

hydrostatic pressure
  pressure exerted by a fluid due to gravity

manometer
  device used to measure the pressure of a gas trapped in a container

pascal (Pa)
  SI unit of pressure; $1 \text{ Pa} = 1 \text{ N/m}^2$

pounds per square inch (psi)
  unit of pressure common in the US

pressure
  force exerted per unit area

torr
  unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
By the end of this section, you will be able to:

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly ([link]), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.
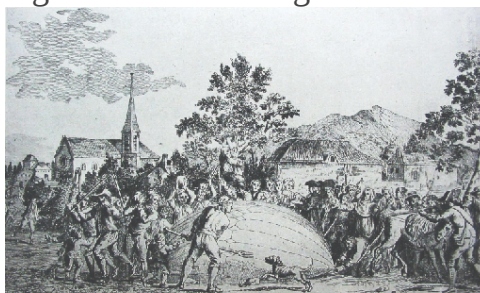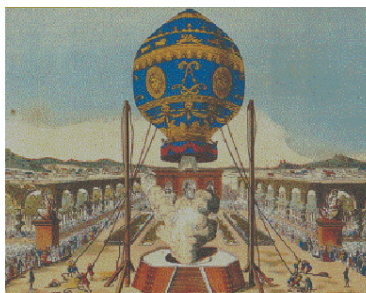
(a)　　　　　　　　　　(b)　　　　　　　　　　(c)

In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is

rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter ([link]) and the pressure increases.
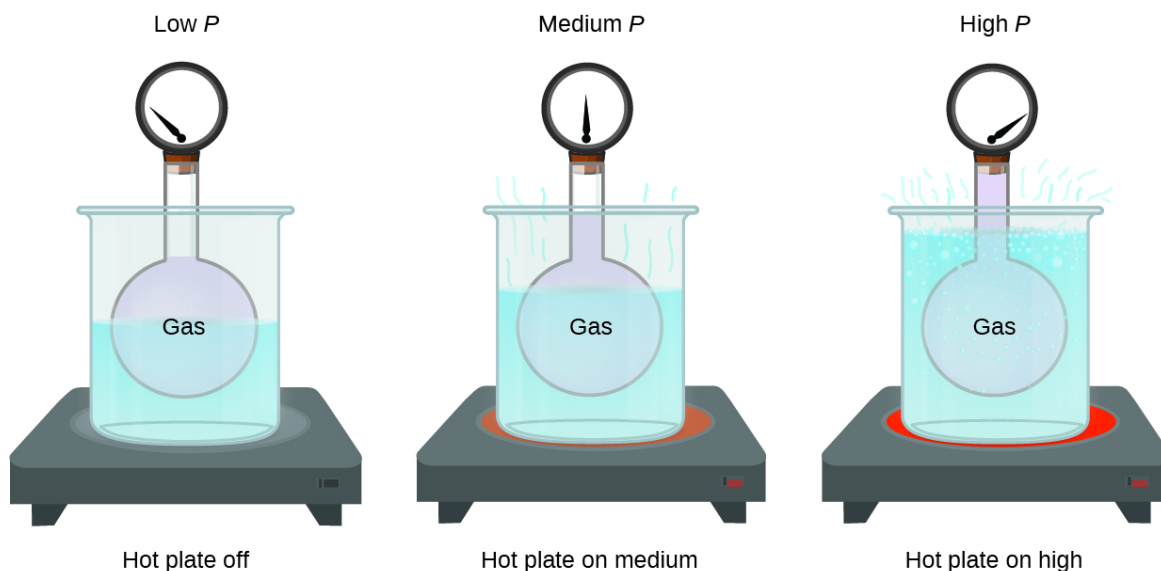
The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in [link]. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
−150	173	36.0
−100	223	46.4
−50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0
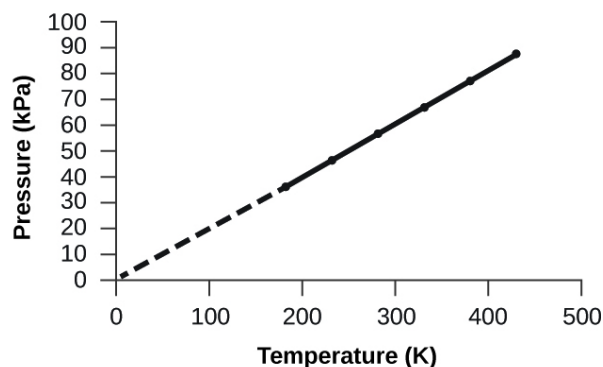
For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at −273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the *P-T* relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:
Equation:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where ∝ means "is proportional to," and *k* is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe

how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example:
Predicting Change in Pressure with Temperature
A can of hair spray is used until it is empty except for the propellant, isobutane gas.
(a) On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
(b) The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?
Solution
(a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)
(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:
Equation:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360\,\text{kPa}}{297\,\text{K}} = \frac{P_2}{323\,\text{K}}$$

Rearranging and solving gives: $P_2 = \frac{360\,\text{kPa} \times 323\,\cancel{\text{K}}}{297\,\cancel{\text{K}}} = 390\,\text{kPa}$
Check Your Learning
A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Note:
Answer:
400 torr

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

Note:

This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in [link].

Temperature (°C)	Temperature (K)	Volume (L)
−3	270	22
−23	250	21
−53	220	18
−162	111	9
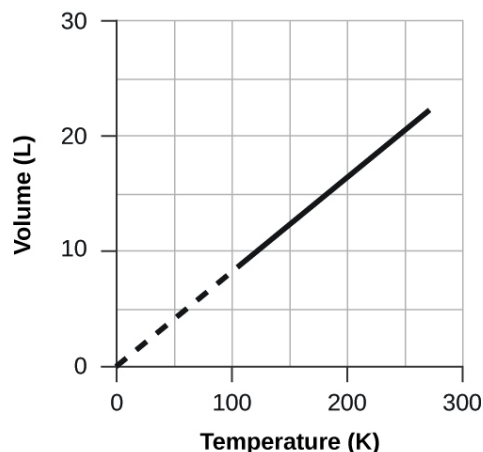
The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant.*

Mathematically, this can be written as:
Equation:

$$V \, \alpha \, T \quad \text{or} \quad V = \text{constant} \cdot T \quad \text{or} \quad V = k \cdot T \quad \text{or} \quad V_1/T_1 = V_2/T_2$$

with *k* being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = *k*), and as seen with the *P-T* relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

Example:
Predicting Change in Volume with Temperature
A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?
Solution
Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:
Equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

Rearranging and solving gives: $V_2 = \frac{0.300\,\text{L} \times 303\,\cancel{\text{K}}}{283\,\cancel{\text{K}}} = 0.321\,\text{L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Check Your Learning

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Note:
Answer:
21.6 mL

Example:
Measuring Temperature with a Volume Change

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

Equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0\,\text{cm}^3}{273.15\,\text{K}} = \frac{131.7\,\text{cm}^3}{T_2}$$

Rearrangement gives $T_2 = \frac{131.7\,\cancel{\text{cm}^3} \times 273.15\,\text{K}}{150.0\,\cancel{\text{cm}^3}} = 239.8\,\text{K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

Check Your Learning

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Note:
Answer:
635 mL

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in [link].
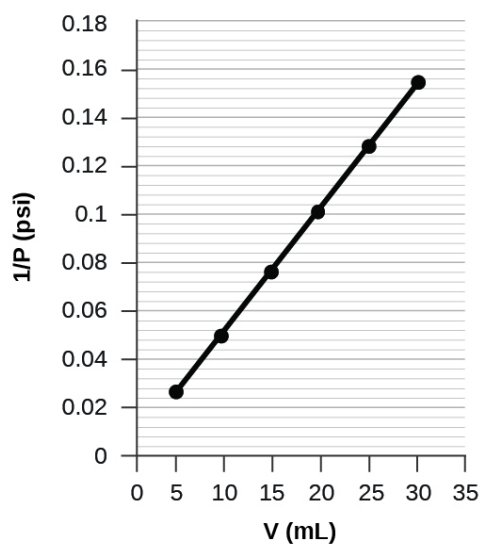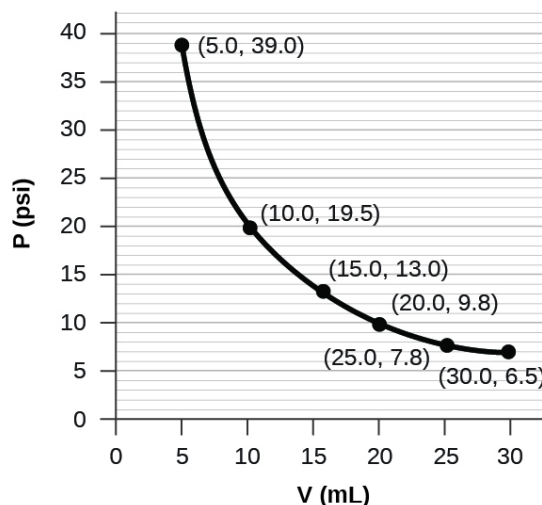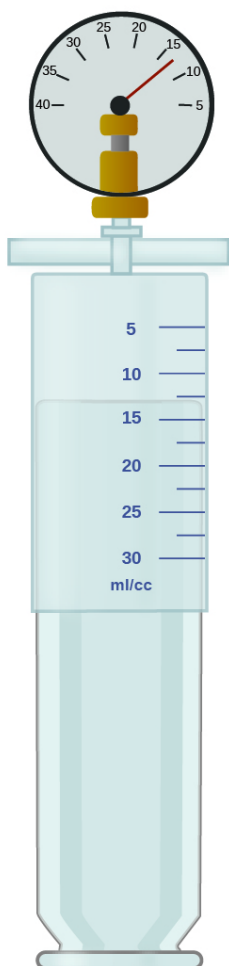
When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear.

Unlike the P-T and V-T relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

Equation:

$$P \, \alpha \, 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1V_1 = P_2V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure $\frac{1}{P}$ versus the volume (V), or the inverse of volume $\frac{1}{V}$ versus the pressure (P). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to "linearize" their data. If we plot P versus V, we obtain a hyperbola.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example:
Volume of a Gas Sample
The sample of gas in [link] has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:
(a) the P-V graph in [link]
(b) the $\frac{1}{P}$ vs. V graph in [link]
(c) the Boyle's law equation
Comment on the likely accuracy of each method.
Solution
(a) Estimating from the P-V graph gives a value for P somewhere around 27 psi.
(b) Estimating from the $\frac{1}{P}$ versus V graph give a value of about 26 psi.
(c) From Boyle's law, we know that the product of pressure and volume (PV) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$. Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:
Equation:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:
Equation:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ mL}}{7.5 \text{ mL}} = 26 \text{ psi}$$

It was more difficult to estimate well from the *P-V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Check Your Learning

The sample of gas in [link] has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

(a) the *P-V* graph in [link]

(b) the $\frac{1}{P}$ vs. *V* graph in [link]

(c) the Boyle's law equation

Comment on the likely accuracy of each method.

Note:
Answer:
(a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the *P-V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Note:
Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life ([link]).

Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.
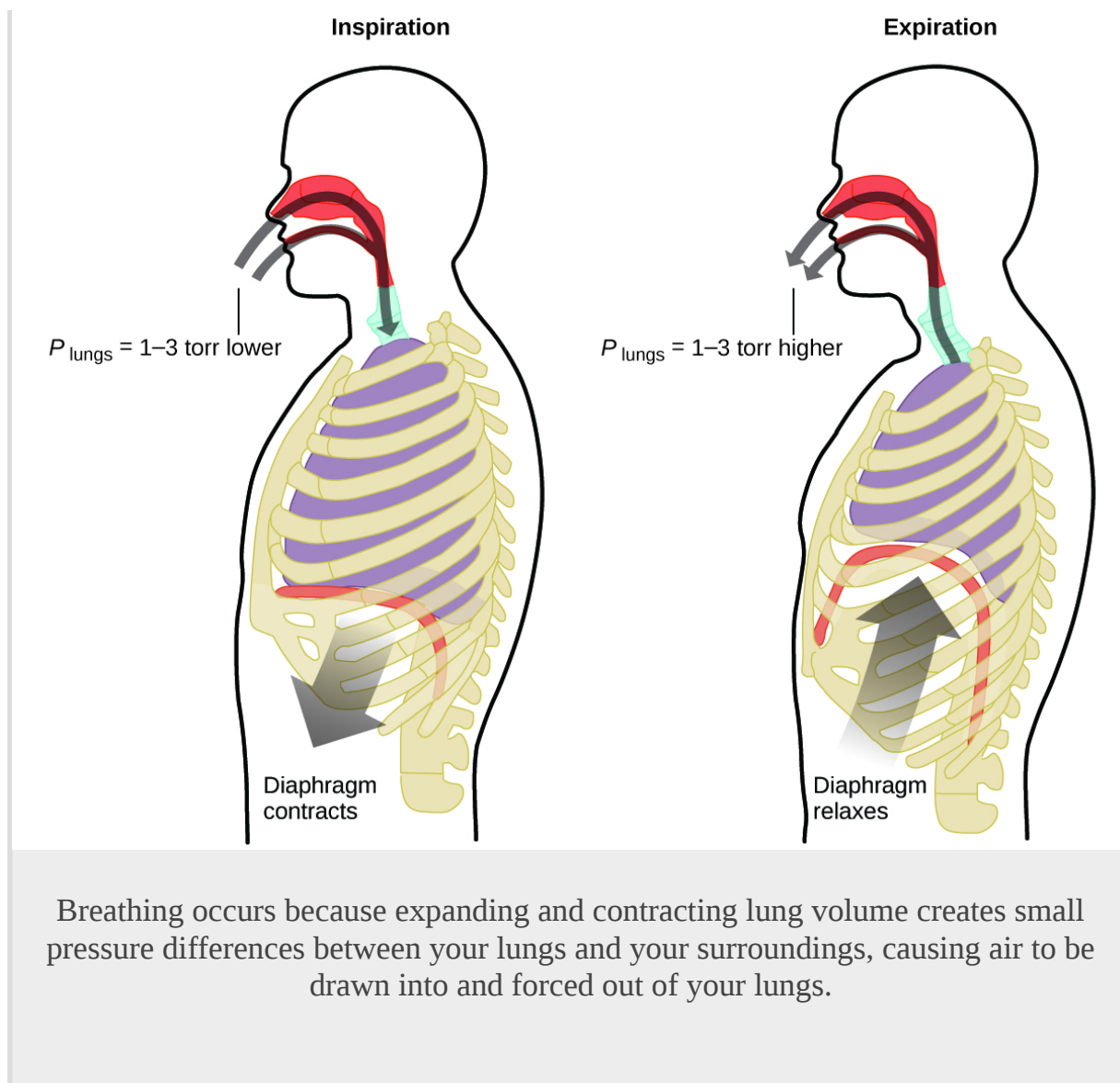
Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:
Equation:

$$V \propto n \quad \text{or} \quad V = k \times n \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as P versus n, and n versus T.

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's law: $\frac{P}{T}$ = constant at constant V and n
- Charles's law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law: $\frac{V}{n}$ = constant at constant P and T

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:
Equation:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the **ideal gas constant**

or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.314 kPa L mol^{-1} K^{-1}.

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example:
Using the Ideal Gas Law
Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?
Solution
We must rearrange $PV = nRT$ to solve for V: $V = \frac{nRT}{P}$
If we choose to use $R = 0.08206$ L atm mol^{-1} K^{-1}, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.
Converting into the "right" units:
Equation:

$$n = 6\,55\ \cancel{\text{g CH}_4} \times \frac{1\,\text{mol}}{16.043\ \cancel{\text{g CH}_4}} = 40.8\,\text{mol}$$

Equation:

$$T = 25\ ^\circ\text{C} + 273 = 298\,\text{K}$$

Equation:

$$P = 745 \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{torr}}} = 0.980 \text{ atm}$$

Equation:

$$V = \frac{nRT}{P} = \frac{(40.8 \cancel{\text{mol}})(0.08206 \text{ L} \cancel{\text{ atm mol}^{-1} \text{K}^{-1}})(298 \cancel{\text{K}})}{0.980 \cancel{\text{atm}}} = 1.02 \times 10^3 \text{L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Check Your Learning

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Note:
Answer:
350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law constant).

Example:
Using the Combined Gas Law
When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm ([link]). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?

Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

Equation:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \longrightarrow \frac{(153 \text{ atm})(13.2 \text{ L})}{(300 \text{ K})} = \frac{(3.13 \text{ atm})(V_2)}{(310 \text{ K})}$$

Solving for V_2:

Equation:

$$V_2 = \frac{(153 \text{ \cancel{atm}})(13.2 \text{ L})(310 \text{ \cancel{K}})}{(300 \text{ \cancel{K}})(3.13 \text{ \cancel{atm}})} = 667 \text{ L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures

and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

Check Your Learning

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Note:
Answer:
0.193 L

Note:
The Interdependence between Ocean Depth and Pressure in Scuba Diving
Whether scuba diving at the Great Barrier Reef in Australia (shown in [link]) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.

Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as "atmospheres absolute" or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body's air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa).

At STP, an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** ([link]).

He (4 g)   NH₃ (15 g)   O₂ (32 g)
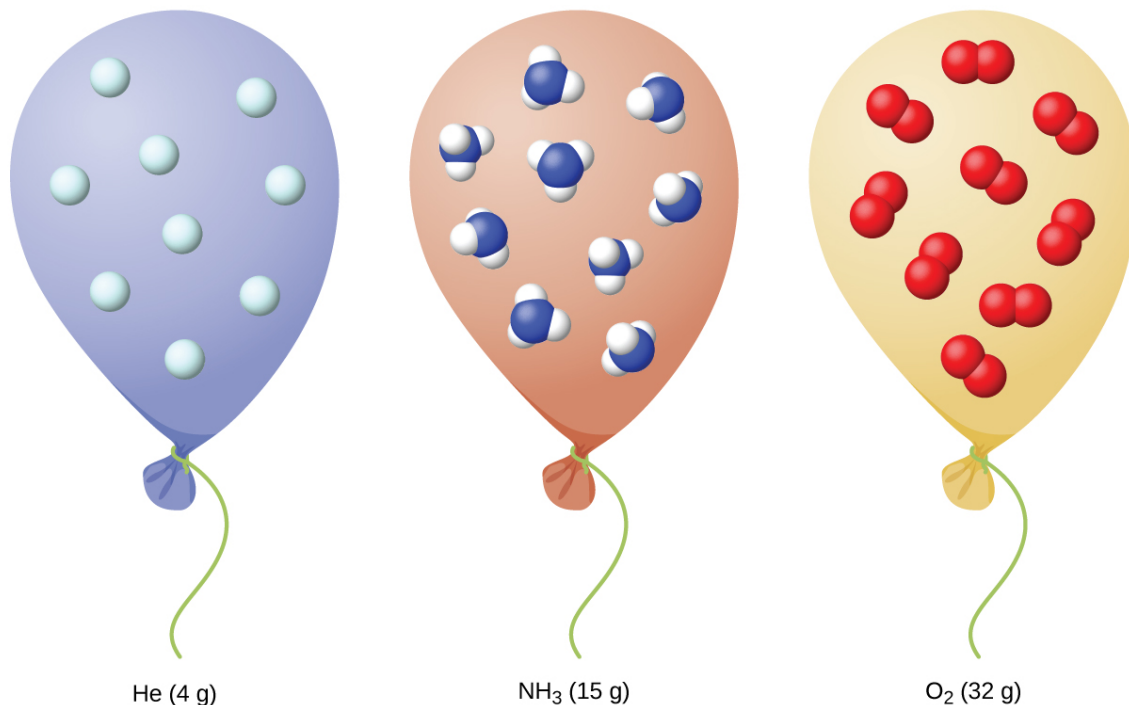
Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

Key Concepts and Summary

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas,

T is its kelvin temperature, and *R* is the ideal (universal) gas constant.

Key Equations

- *PV = nRT*

Chemistry End of Chapter Exercises

Exercise:

  Problem:

  Sometimes leaving a bicycle in the sun on a hot day will cause a blowout. Why?

Exercise:

  Problem:

  Explain how the volume of the bubbles exhausted by a scuba diver ([link]) change as they rise to the surface, assuming that they remain intact.

  Solution:

  As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

Exercise:

  Problem:

  One way to state Boyle's law is "All other things being equal, the pressure of a gas is inversely proportional to its volume." (a) What is the meaning of the term "inversely proportional?" (b) What are the "other things" that must be equal?

Exercise:

  Problem:

  An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas." (a) What is the meaning of the term "directly proportional?" (b) What are the "other things" that must be equal?

  Solution:

(a) The number of particles in the gas increases as the volume increases. (b) temperature, pressure

Exercise:

Problem:

How would the graph in [link] change if the number of moles of gas in the sample used to determine the curve were doubled?

Exercise:

Problem:

How would the graph in [link] change if the number of moles of gas in the sample used to determine the curve were doubled?

Solution:

The curve would be farther to the right and higher up, but the same basic shape.

Exercise:

Problem:

In addition to the data found in [link], what other information do we need to find the mass of the sample of air used to determine the graph?

Exercise:

Problem:

Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using [link].

Solution:

16.3 to 16.5 L

Exercise:

Problem:

Determine the pressure of the gas in the syringe shown in [link] when its volume is 12.5 mL, using:

(a) the appropriate graph

(b) Boyle's law

Exercise:

Problem:

A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can?

Solution:

3.40×10^3 torr

Exercise:

Problem:

What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

Exercise:

Problem:

A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

Solution:

12.1 L

Exercise:

Problem:

A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

Exercise:

Problem:

A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?

Solution:

217 L

Exercise:

Problem:

How many moles of gaseous boron trifluoride, BF_3, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3?

Solution:

8.190×10^{-2} mol; 5.553 g

Exercise:

Problem: How many grams of gas are present in each of the following cases?

(a) 0.100 L of CO_2 at 307 torr and 26 °C

(b) 8.75 L of C_2H_4, at 378.3 kPa and 483 K

(c) 221 mL of Ar at 0.23 torr and –54 °C

Solution:

(a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g

Exercise:

Problem:

A high altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21 °C and a pressure of 745 torr. What is the volume of the balloon at a height of 20 km, where the temperature is –48 °C and the pressure is 63.1 torr?

Exercise:

Problem:

A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

Solution:

5561 L

Exercise:

Problem:

While resting, the average 70-kg human male consumes 14 L of pure O_2 per hour at 25 °C and 100 kPa. How many moles of O_2 are consumed by a 70 kg man while resting for 1.0 h?

Exercise:

Problem:

For a given amount of gas showing ideal behavior, draw labeled graphs of:

(a) the variation of P with V

(b) the variation of V with T

(c) the variation of P with T

(d) the variation of $\frac{1}{P}$ with V

Solution:

For a gas exhibiting ideal behavior:

Pressure (y-axis), **Volume** (x-axis), constant n & T
(a)

Volume (y-axis), **Temperature** (x-axis), constant n & P
(b)

Pressure (y-axis), **Temperature** (x-axis), constant n & V
(c)

$\frac{1}{P}$ (y-axis), **Volume** (x-axis), constant n & T
(d)
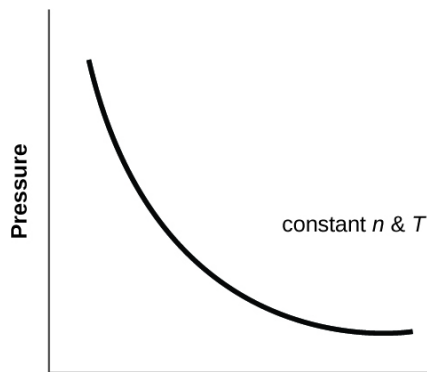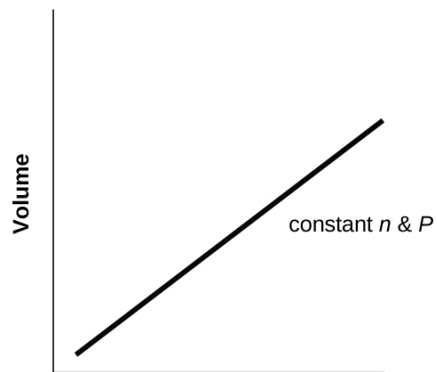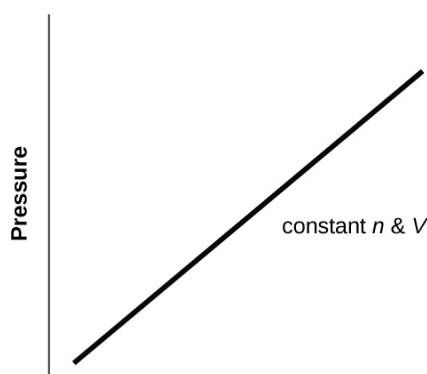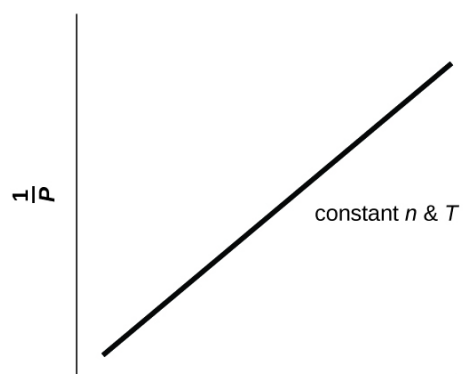
Exercise:

Problem:

A liter of methane gas, CH_4, at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas, H_2, at STP. Using Avogadro's law as a starting point, explain why.

Exercise:

Problem:

The effect of chlorofluorocarbons (such as CCl_2F_2) on the depletion of the ozone layer is well known. The use of substitutes, such as $CH_3CH_2F(g)$, for the chlorofluorocarbons, has largely corrected the problem. Calculate the volume occupied by 10.0 g of each of these compounds at STP:

(a) $CCl_2F_2(g)$

(b) $CH_3CH_2F(g)$

Solution:

(a) 1.85 L CCl_2F_2; (b) 4.66 L CH_3CH_2F

Exercise:

Problem:

As 1 g of the radioactive element radium decays over 1 year, it produces 1.16×10^{18} alpha particles (helium nuclei). Each alpha particle becomes an atom of helium gas. What is the pressure in pascal of the helium gas produced if it occupies a volume of 125 mL at a temperature of 25 °C?

Exercise:

Problem:

A balloon that is 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?

Solution:

0.644 atm

Exercise:

Problem:

If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

Exercise:

Problem:

If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

Solution:

The pressure decreases by a factor of 3.

Glossary

absolute zero
    temperature at which the volume of a gas would be zero according to Charles's
    law.

Amontons's law
    (also, Gay-Lussac's law) pressure of a given number of moles of gas is directly
    proportional to its kelvin temperature when the volume is held constant

Avogadro's law
    volume of a gas at constant temperature and pressure is proportional to the
    number of gas molecules

Boyle's law
    volume of a given number of moles of gas held at constant temperature is
    inversely proportional to the pressure under which it is measured

Charles's law
    volume of a given number of moles of gas is directly proportional to its kelvin
    temperature when the pressure is held constant

ideal gas
    hypothetical gas whose physical properties are perfectly described by the gas
    laws

ideal gas constant (R)
    constant derived from the ideal gas equation $R = 0.08226$ L atm mol^{-1} K^{-1} or
    8.314 L kPa mol^{-1} K^{-1}

ideal gas law
    relation between the pressure, volume, amount, and temperature of a gas under
    conditions derived by combination of the simple gas laws

standard conditions of temperature and pressure (STP)
    273.15 K (0 °C) and 1 atm (101.325 kPa)

standard molar volume
    volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

The Kinetic-Molecular Theory

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the

KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure ([link]).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas ([link]).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions ([link]).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the

total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.
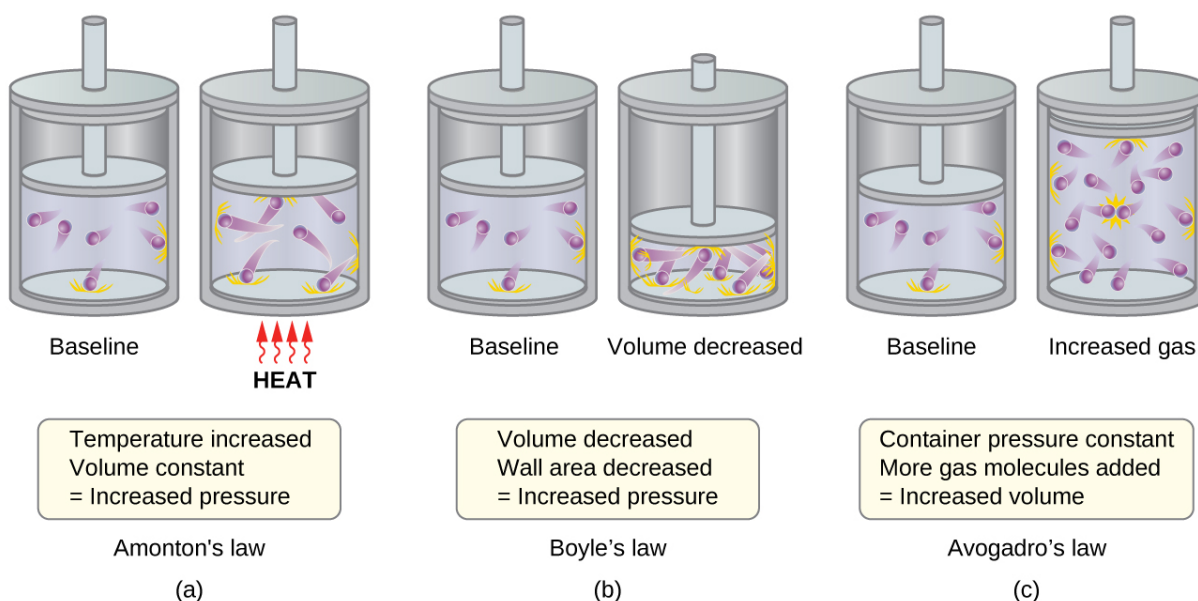
(a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed ([link]).
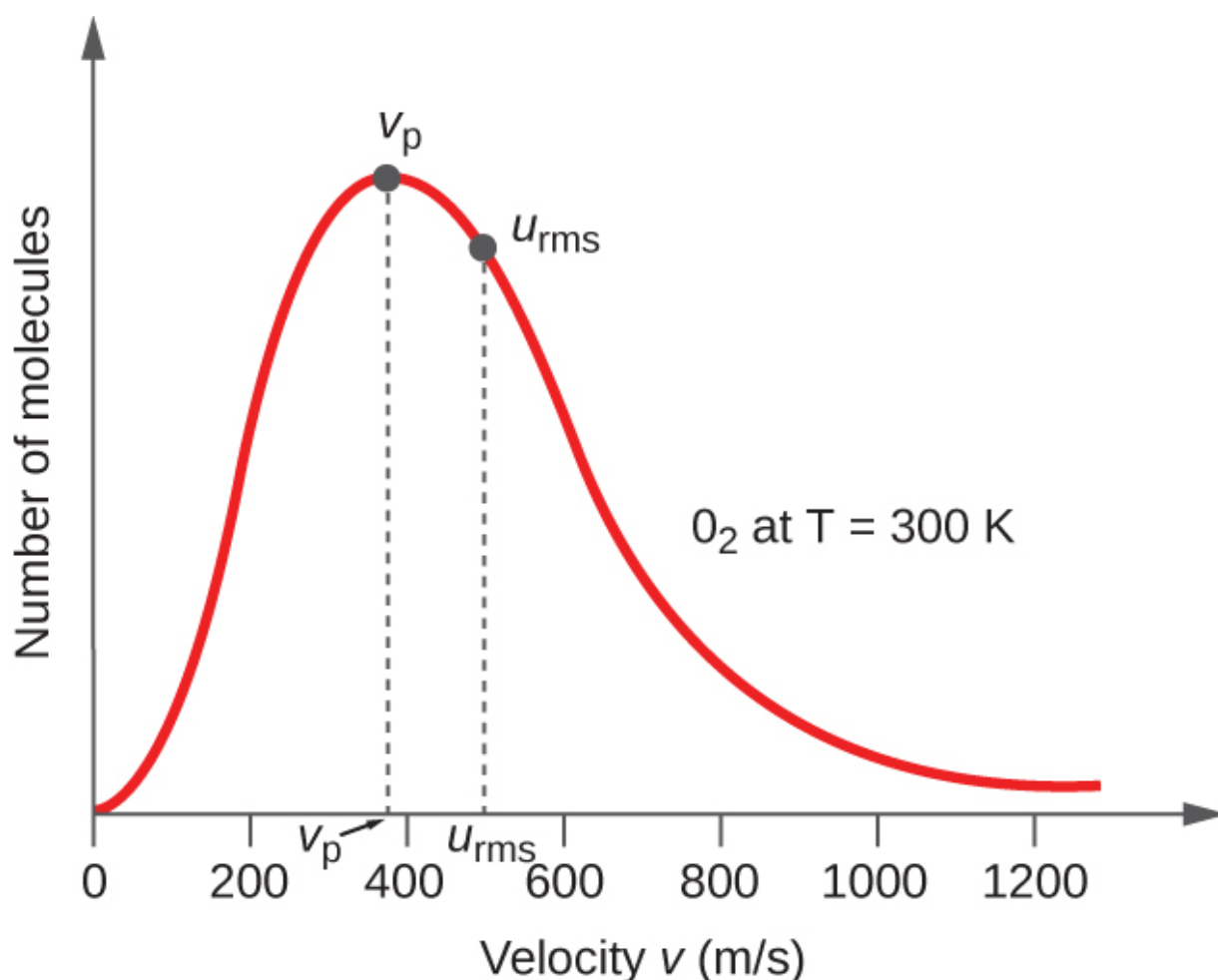
The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:
Equation:

$$\text{KE} = \frac{1}{2}\, m u^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules ($J = kg\ m^2\ s^{-2}$).

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in [link].
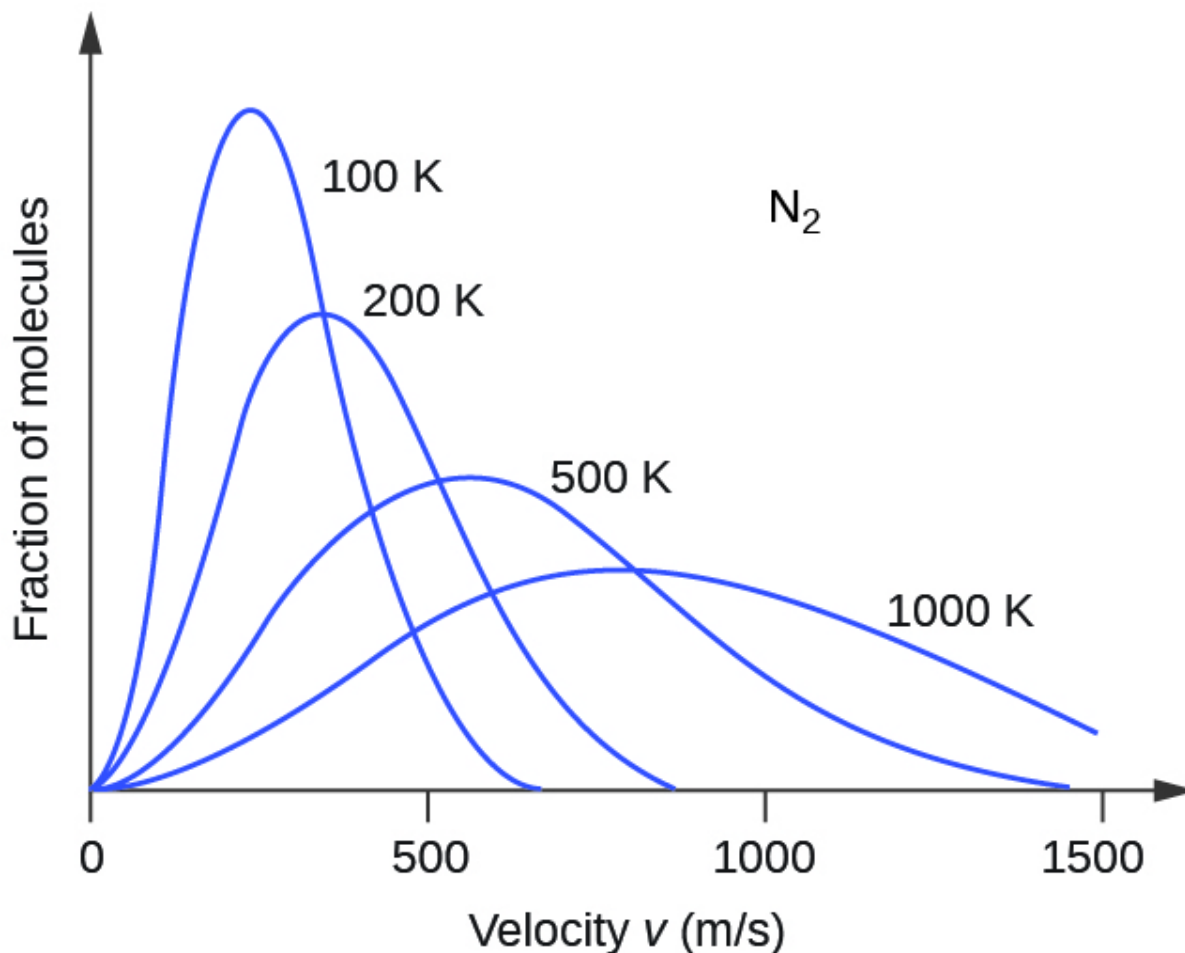
The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms}, with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in [link].
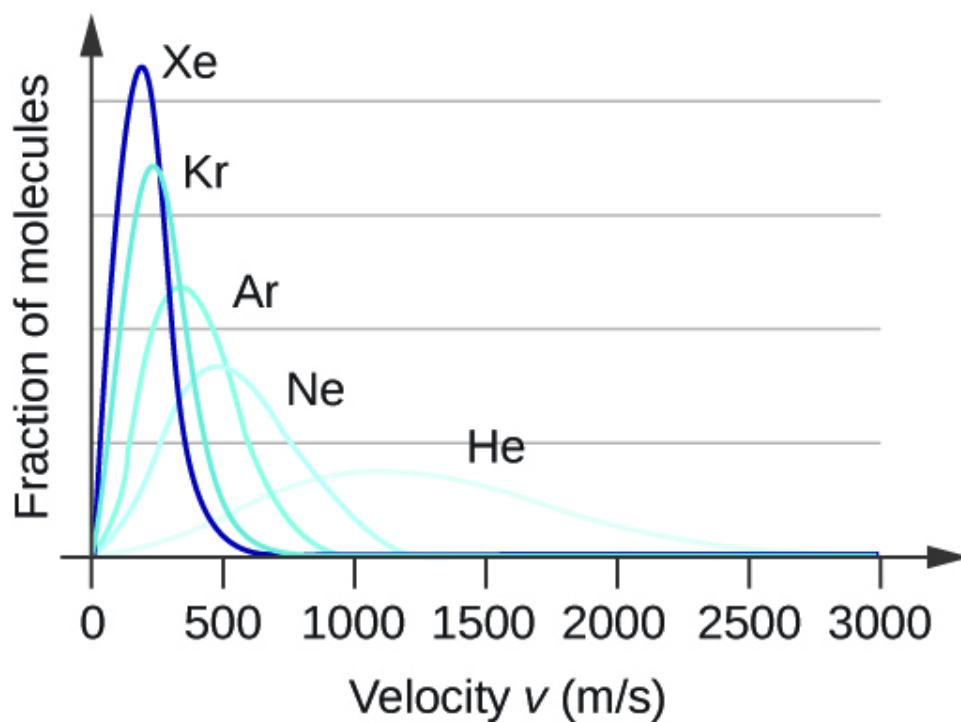
Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

average speed values) for molecules of different masses at various temperatures.

Key Concepts and Summary

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

Chemistry End of Chapter Exercises

Exercise:

Problem:

Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

Exercise:

Problem:

Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

Solution:

Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

Exercise:

Problem:

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

(a) The pressure of the gas is increased by reducing the volume at constant temperature.

(b) The pressure of the gas is increased by increasing the temperature at constant volume.

(c) The average velocity of the molecules is increased by a factor of 2.

Exercise:

Problem:

What is the ratio of the average kinetic energy of a SO_2 molecule to that of an O_2 molecule in a mixture of two gases?

Exercise:

Problem:

A 1-L sample of CO initially at STP is heated to 546 °C, and its volume is increased to 2 L.

(a) What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?

(b) What is the effect on the average kinetic energy of the molecules?

(c) What is the effect on the root mean square speed of the molecules?

Solution:

(a) The number of collisions per unit area of the container wall is constant. (b) The average kinetic energy doubles. (c) The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to $\overline{KE_{avg}}$.

Exercise:

Problem: Answer the following questions:

(a) Is the pressure of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

(b) Is the density of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

(c) At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?

(d) The average temperature of the gas in a hot air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.

(e) The lifting capacity of a hot air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?

(f) An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft^3. What is the lifting power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?

(g) A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO_2 and H_2O gas is produced by the combustion of this propane?

(h) A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?

Solution:

(a) equal; (b) less than; (c) 29.48 g mol^{-1}; (d) 1.0966 g L^{-1}; (e) 0.129 g/L; (f) 4.01×10^5 g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min^{-1}

Glossary

kinetic molecular theory
> theory based on simple principles and assumptions that effectively explains ideal gas behavior

root mean square velocity (u_{rms})
> measure of average velocity for a group of particles calculated as the square root of the average squared velocity

Non-Ideal Gas Behavior
By the end of this section, you will be able to:

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility (Z) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of $PV = nRT$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, V_m) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor (Z)** with:
Equation:

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. [link] shows plots of Z over a large pressure range for several common gases.
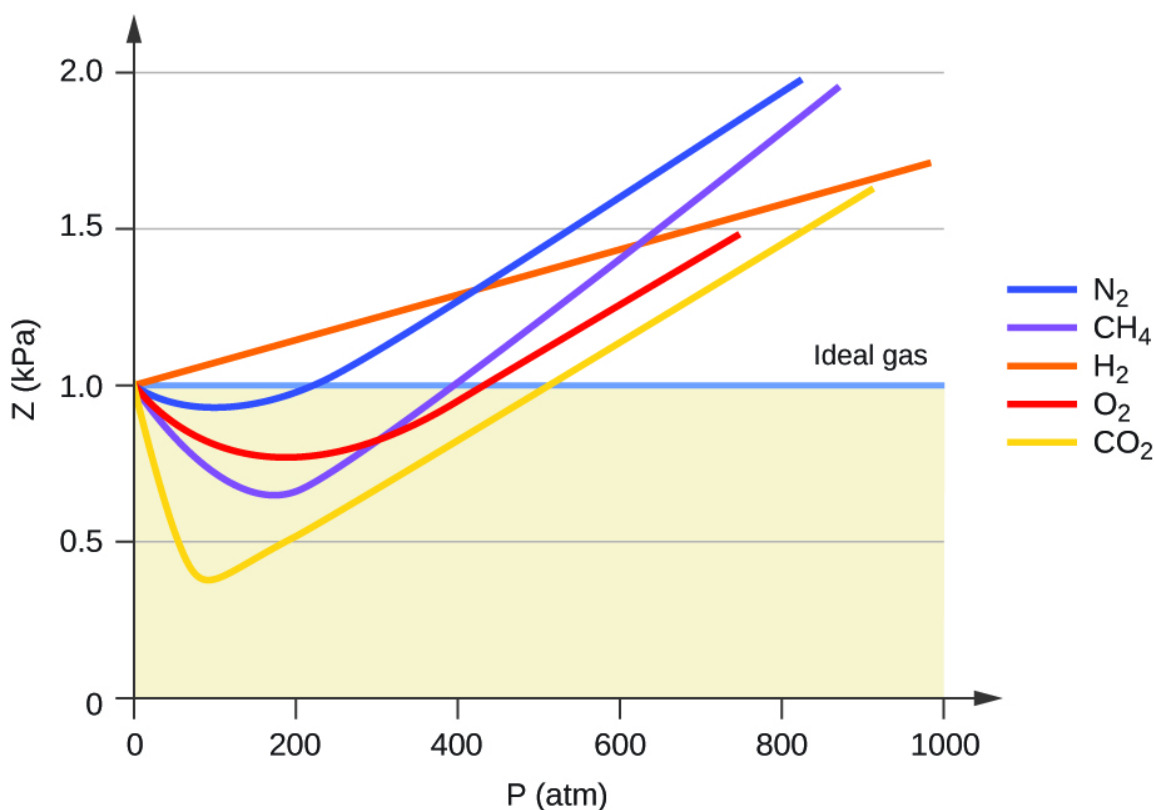
A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

As is apparent from [link], the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas ([link]). The gas therefore

becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.
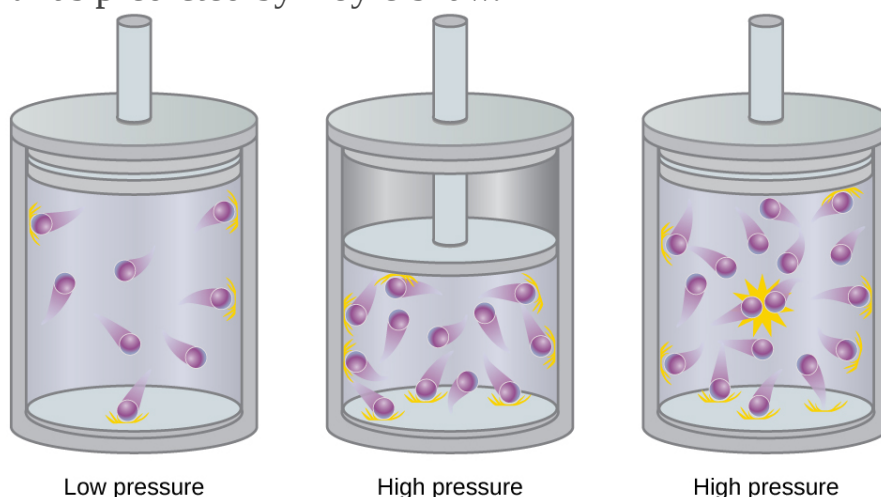
Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) ([link]). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.
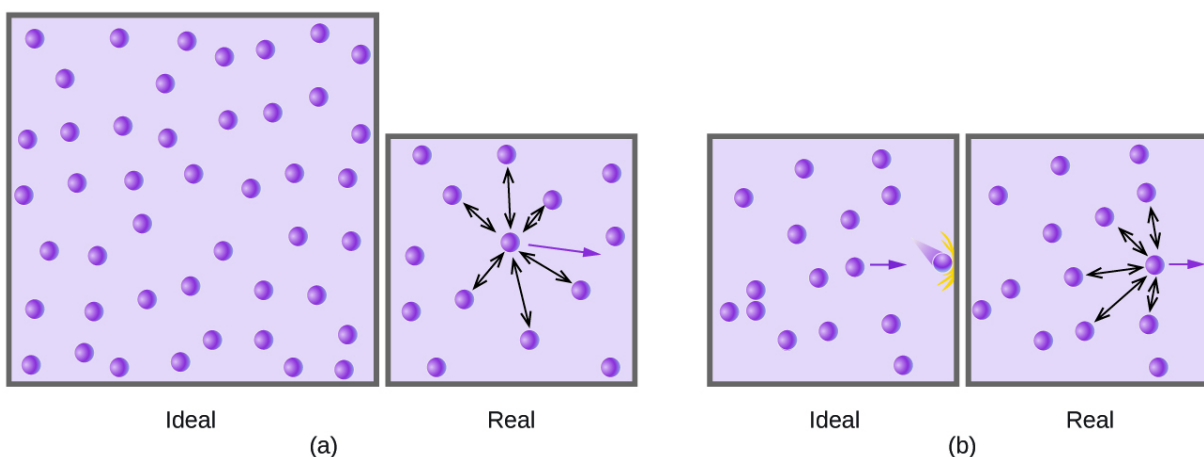
(a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Correction for molecular attraction

Correction for volume of molecules

The constant a corresponds to the strength of the attraction between molecules of a particular gas, and the constant b corresponds to the size of the molecules of a particular gas. The "correction" to the pressure term in the ideal gas law is —— and the "correction" to the volume is nb. Note that

when V is relatively large and n is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, $PV = nRT$. Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in [link].

Values of van der Waals Constants for Some Common Gases		
Gas	a (L^2 atm/mol^2)	b (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

At low pressures, the correction for intermolecular attraction, a, is more important than the one for molecular volume, b. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV = nRT$ over a small range of pressures. This behavior is reflected by the "dips" in several of the compressibility curves shown in [link]. The attractive force between

molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing *P*). At very high pressures, the gas becomes less compressible (Z increases with *P*), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Key Concepts and Summary

Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behavior is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behavior, and the gas is said to exhibit ideal behavior. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behavior of gases under these conditions.

Key Equations

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Chemistry End of Chapter Exercises

Exercise:

Problem:

Explain why the plot of PV for CO_2 differs from that of an ideal gas.
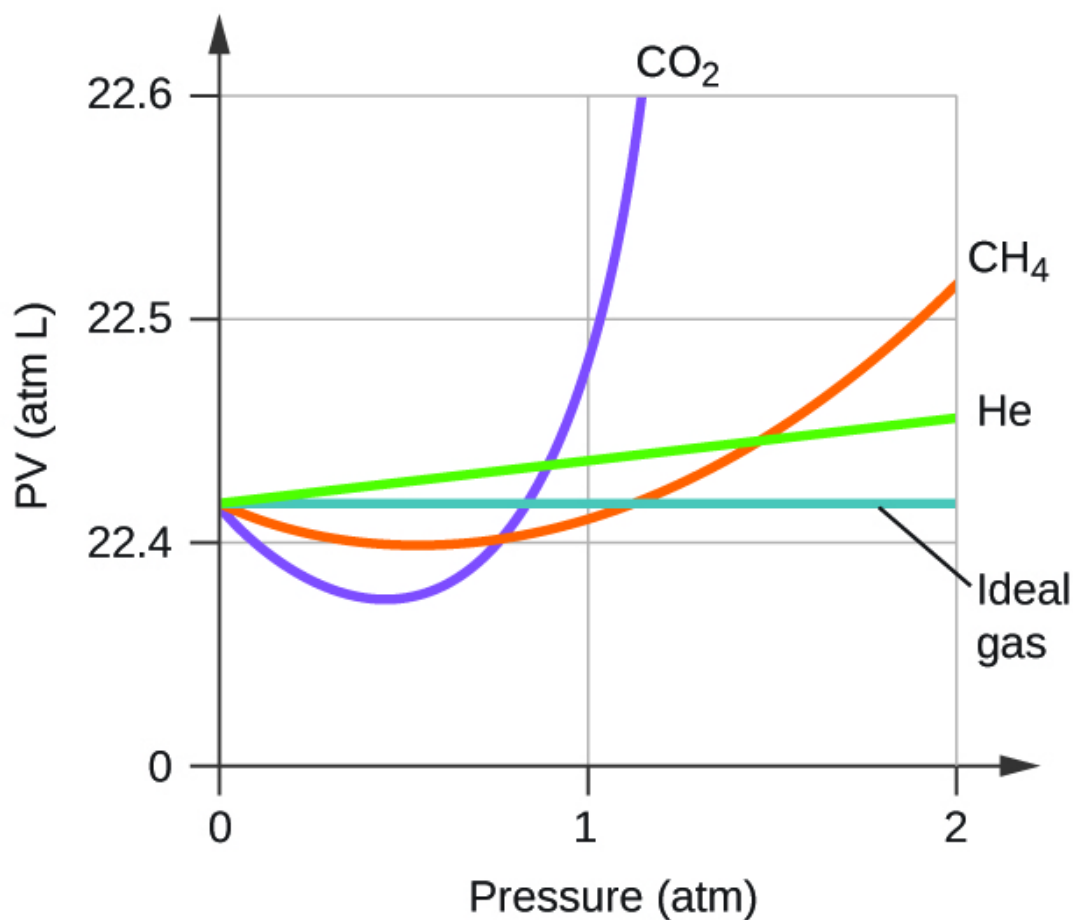
Exercise:

Problem:

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

(a) high pressure, small volume

(b) high temperature, low pressure

(c) low temperature, high pressure

Solution:

The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

Exercise:

Problem:

Describe the factors responsible for the deviation of the behavior of real gases from that of an ideal gas.

Exercise:

Problem:

For which of the following gases should the correction for the molecular volume be largest:

CO, CO_2, H_2, He, NH_3, SF_6?

Solution:

SF_6

Exercise:

Problem: Answer the following questions:

(a) If XX behaved as an ideal gas, what would its graph of Z vs. P look like?

(b) For most of this chapter, we performed calculations treating gases as ideal. Was this justified?

(c) What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.

(d) What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.

(e) In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

Solution:

(a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see [link]) (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. See [link]. (e) low temperatures

Glossary

compressibility factor (Z)
    ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

van der Waals equation

    modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Introduction
class="introduction"

- Intermolecular Forces
- Properties of Liquids
- Phase Transitions
- Phase Diagrams
- The Solid State of Matter
- Lattice Structures in Crystalline Solids

Solid carbon dioxide ("dry ice", left) sublimes vigorously when placed in a liquid (right), cooling the liquid and generating a fog of condensed water vapor above the cylinder. (credit: modification of work by Paul Flowers)

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

Intermolecular Forces
By the end of this section, you will be able to:

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy

required to overcome the attractive forces and thus increase the distance between particles. [link] illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.
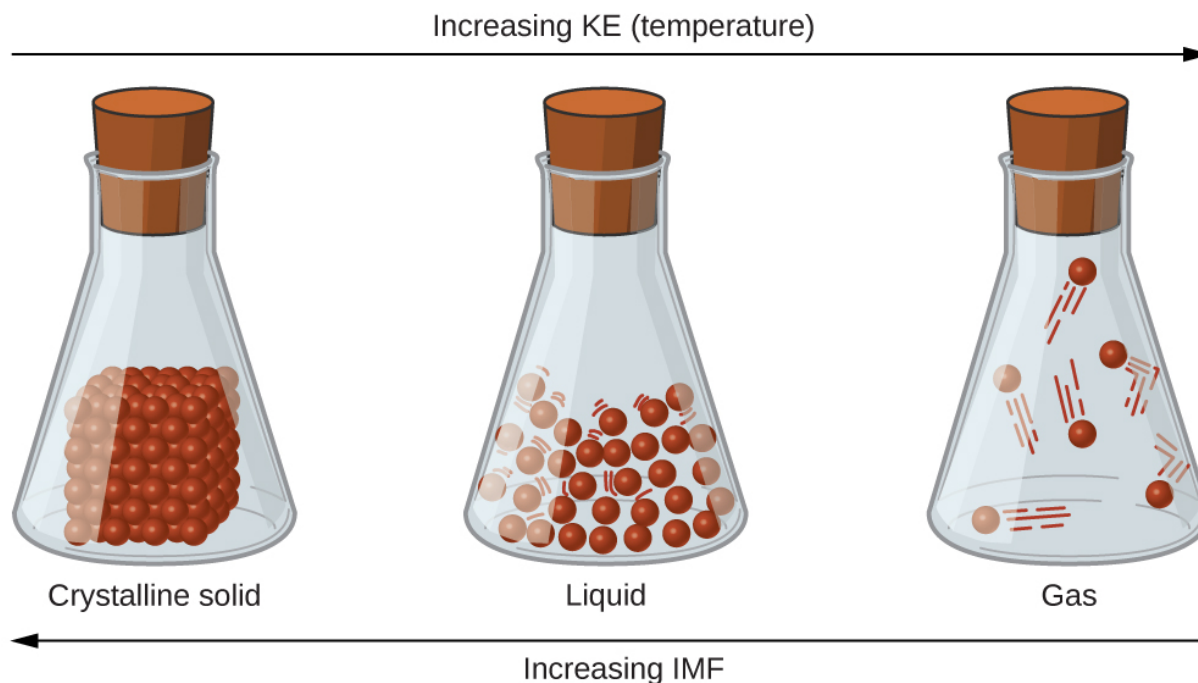
Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in [link].

Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in [link].

Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. [link] illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of

liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy— 430 kilojoules.
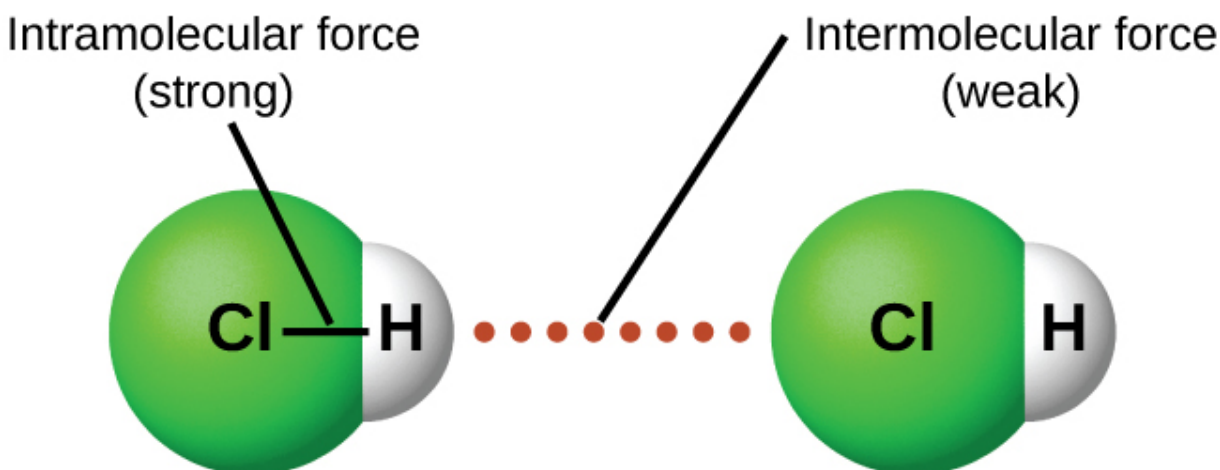
*Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or,

alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in [link].
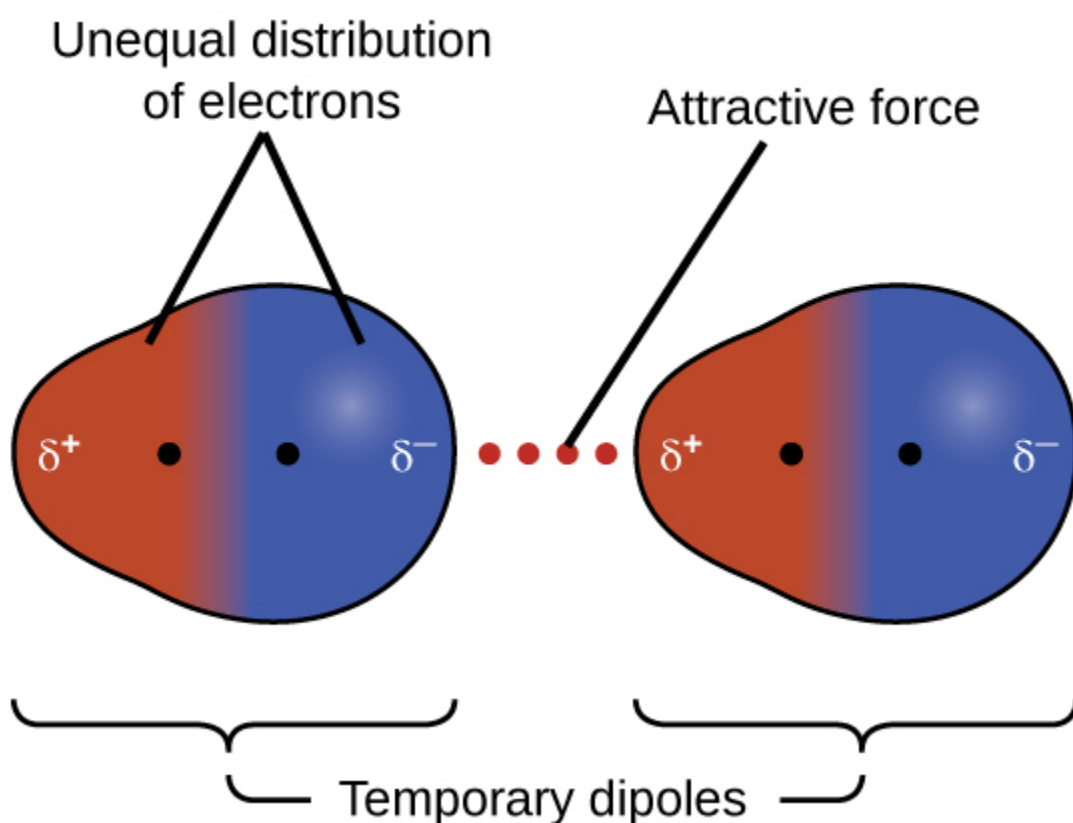
Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak,

however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in [link].

Melting and Boiling Points of the Halogens				
Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average,

farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example:
London Forces and Their Effects
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.
Solution
Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 < SiH_4 < GeH_4 < SnH_4$.
A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:

Carbon Family
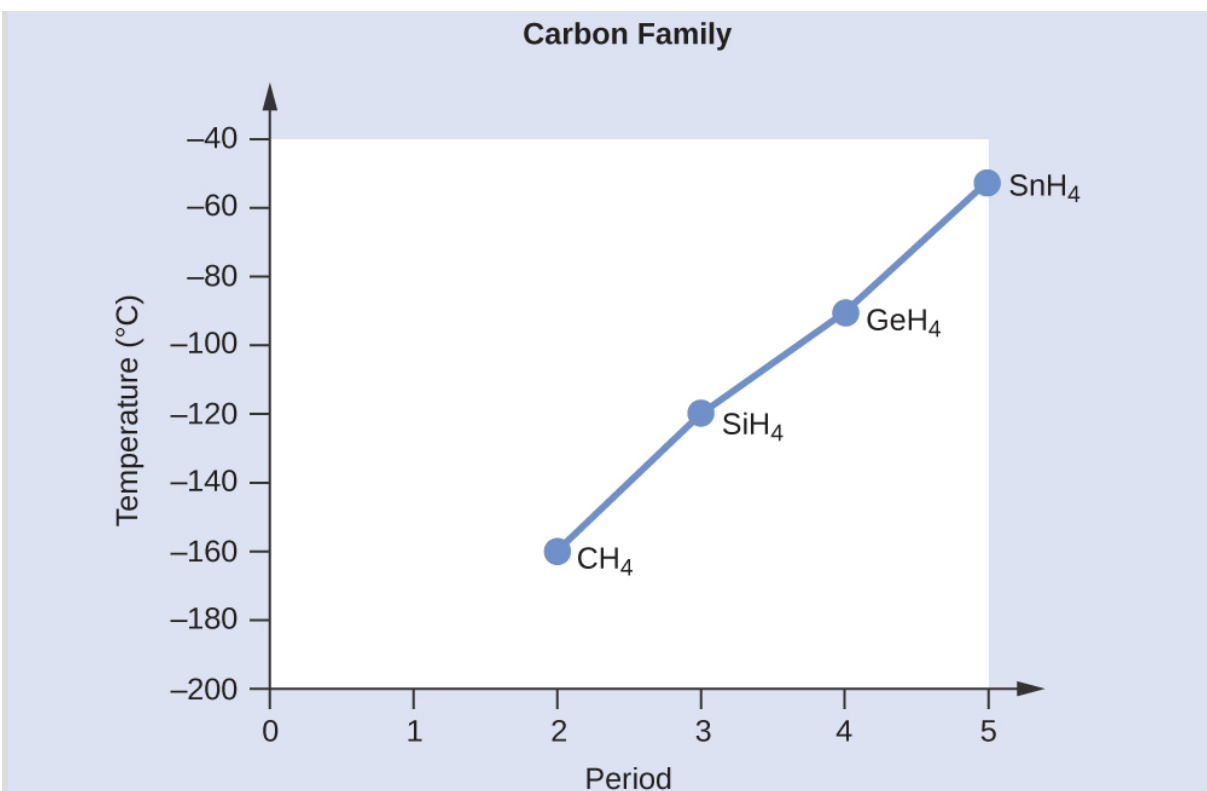
Check Your Learning
Order the following hydrocarbons from lowest to highest boiling point:
C_2H_6, C_3H_8, and C_4H_{10}.

Note:
Answer:
$C_2H_6 < C_3H_8 < C_4H_{10}$. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore $C_2H_6 < C_3H_8 < C_4H_{10}$.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane,

isopentane, and neopentane (shown in [link]) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

Small contact area, weakest attraction	Less surface area, less attraction	Large contact area, strong attraction
neopentane boiling point: 9.5 °C	isopentane boiling point: 27 °C	*n*-pentane boiling point: 36 °C
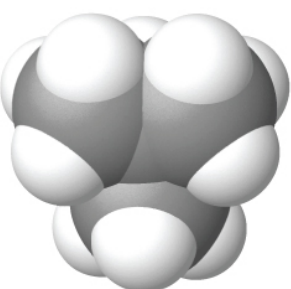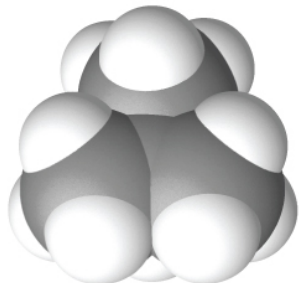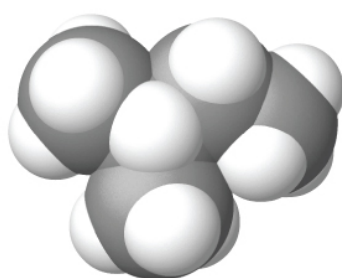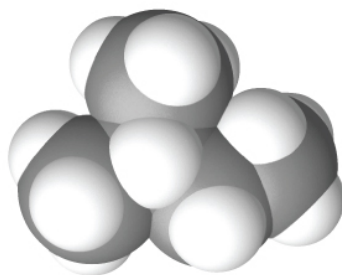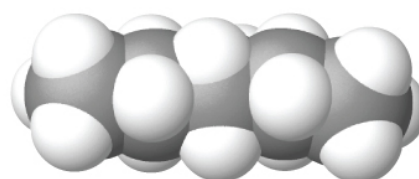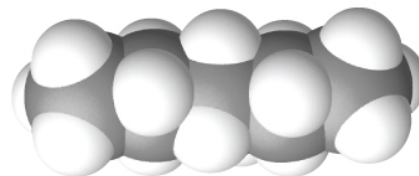
The strength of the dispersion forces increases with the contact area

between molecules, as demonstrated by the boiling points of these pentane isomers.

Note:

Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in [link], with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily

move across it. Further investigations may eventually lead to the development of better adhesives and other applications.
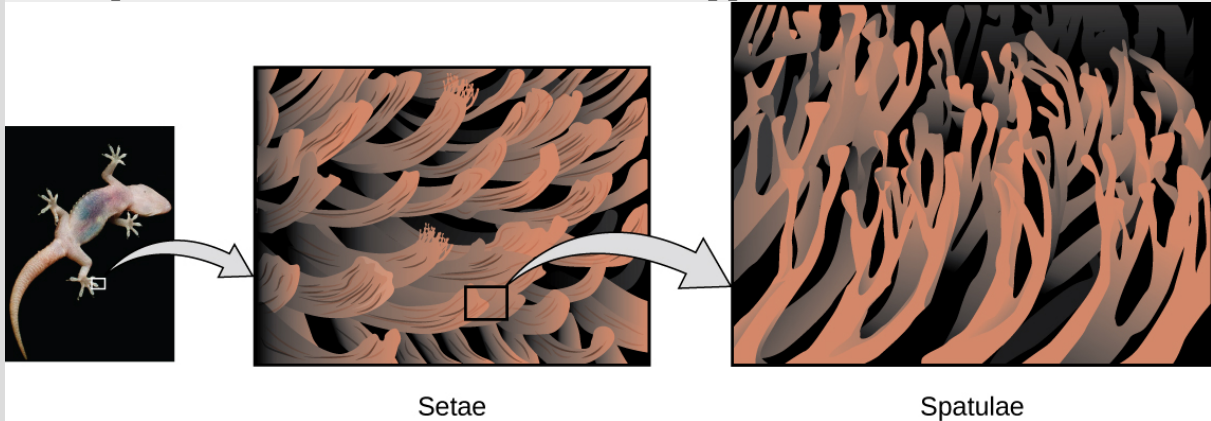
Setae   Spatulae

Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

Note:

Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a **dipole-dipole attraction**—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in [link].
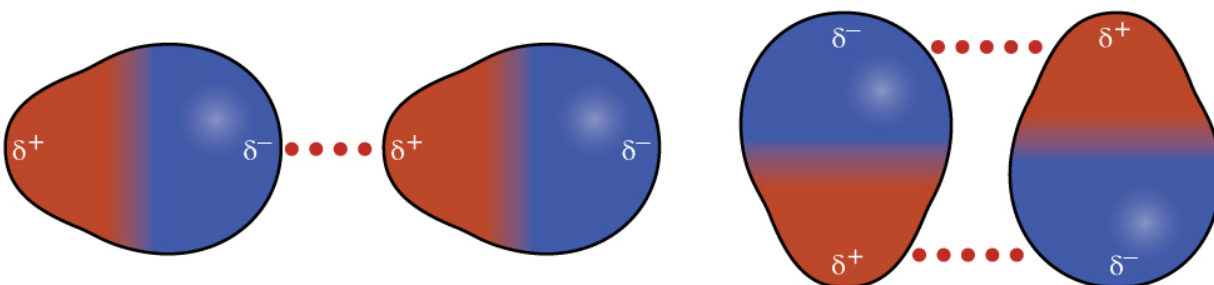
This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this

temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example:
Dipole-Dipole Forces and Their Effects
Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.
Solution
CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.
Check Your Learning
Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Note:
Answer:
ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include HF⋯HF, H_2O⋯HOH, and H_3N⋯HNH_2, in which the hydrogen bonds are denoted by dots. [link] illustrates hydrogen bonding between water molecules.
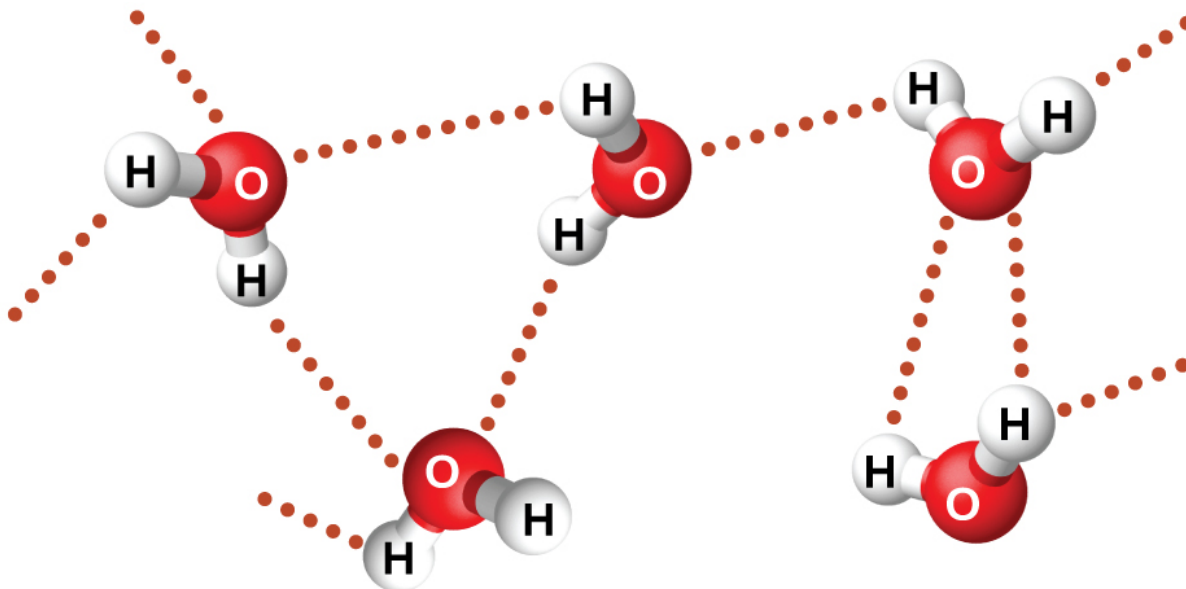
Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in [link]. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.
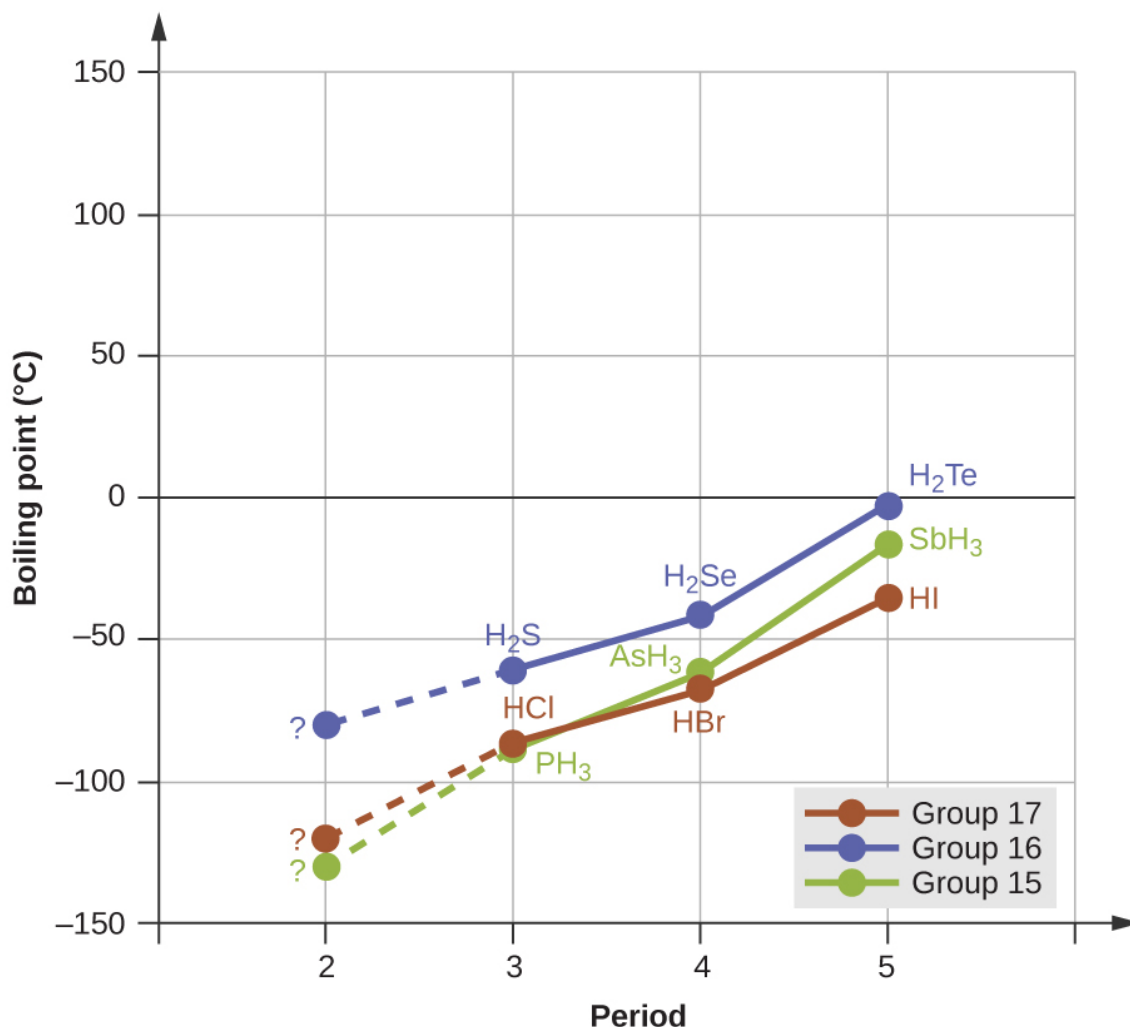
For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in [link]. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.
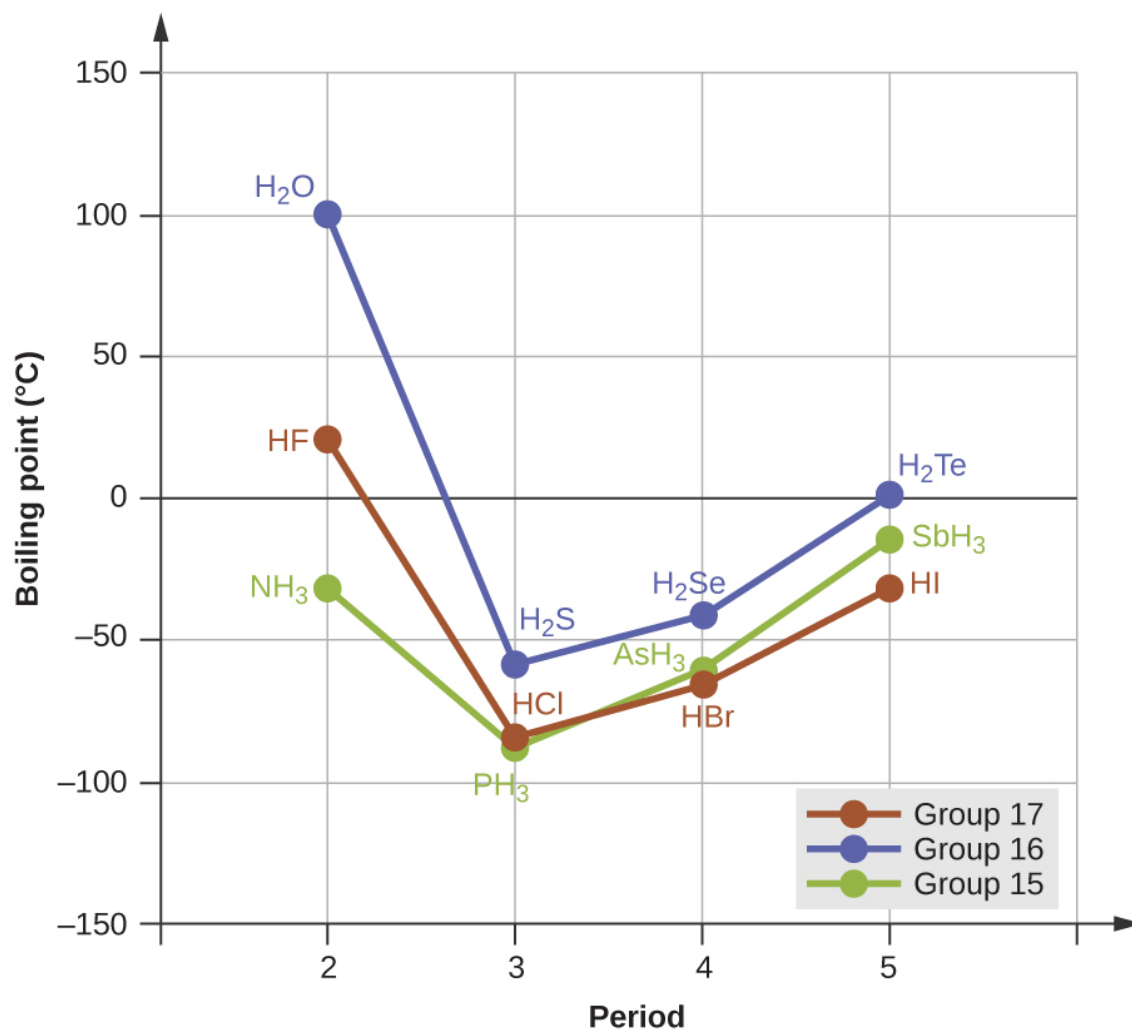
In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

Example:
Effect of Hydrogen Bonding on Boiling Points
Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not

necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Check Your Learning

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Note:

Answer:

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Note:

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in [link].
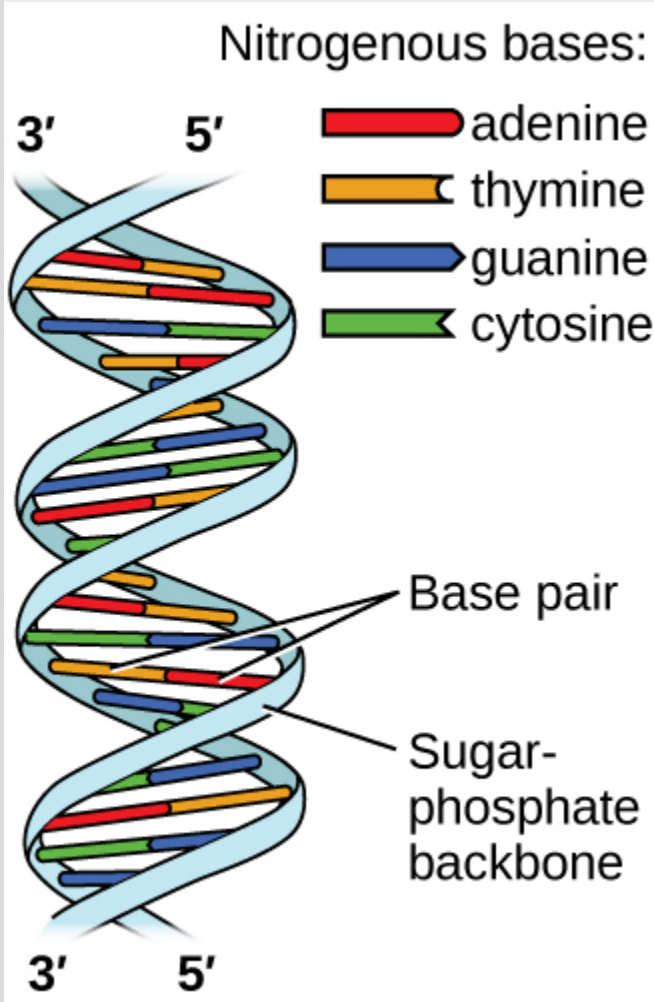
Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure [link].
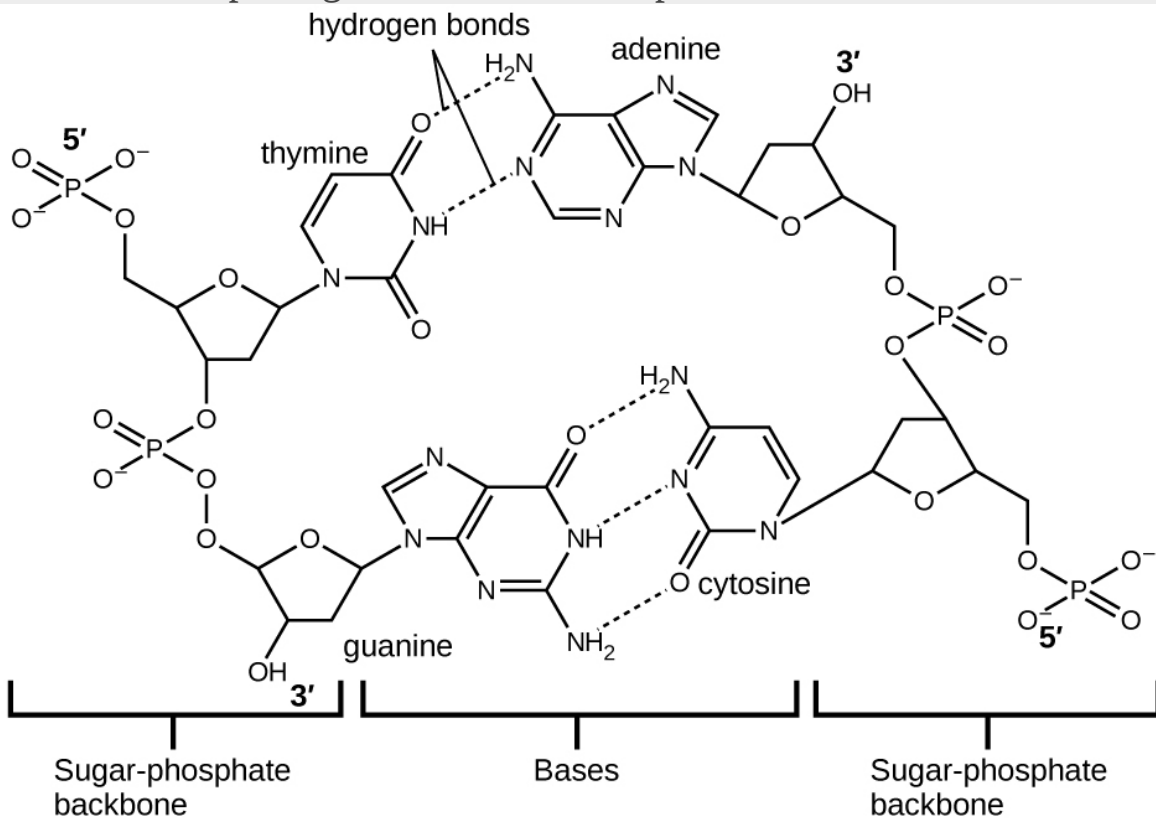
The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are

relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Key Concepts and Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Chemistry End of Chapter Exercises

Exercise:

Problem:

In terms of their bulk properties, how do liquids and solids differ? How are they similar?

Solution:

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar

densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

Exercise:

Problem:

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

Exercise:

Problem:

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

Solution:

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

Exercise:

Problem:

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

Exercise:

Problem:

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

Solution:

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

Exercise:

Problem:

Open the [PhET States of Matter Simulation](#) to answer the following questions:

(a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?

(b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.

(c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

Exercise:

Problem: Define the following and give an example of each:

(a) dispersion force

(b) dipole-dipole attraction

(c) hydrogen bond

Solution:

(a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar). (b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICI molecules attract one another by dipole-dipole interaction). (c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: $HF\cdots HF$).

Exercise:

Problem:

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

Exercise:

Problem:

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

Solution:

The London forces typically increase as the number of electrons increase.

Exercise:

Problem:

Neon and HF have approximately the same molecular masses.

(a) Explain why the boiling points of Neon and HF differ.

(b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

Exercise:

Problem:

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

(a) HCl, H_2O, SiH_4

(b) F_2, Cl_2, Br_2

(c) CH_4, C_2H_6, C_3H_8

(d) O_2, NO, N_2

Solution:

(a) $SiH_4 < HCl < H_2O$; (b) $F_2 < Cl_2 < Br_2$; (c) $CH_4 < C_2H_6 < C_3H_8$; (d) $N_2 < O_2 < NO$

Exercise:

Problem:

The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer.

Solution:

−85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.

Exercise:

Problem:

Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

Exercise:

Problem:

Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

Solution:

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

Exercise:

Problem:

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

Exercise:

Problem:

Identify the intermolecular forces present in the following solids:

(a) CH_3CH_2OH

(b) $CH_3CH_2CH_3$

(c) CH_3CH_2Cl

Solution:

(a) hydrogen bonding and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

Glossary

dipole-dipole attraction
    intermolecular attraction between two permanent dipoles

dispersion force
    (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding
    occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole
    temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole
    temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force
    noncovalent attractive force between atoms, molecules, and/or ions

polarizability
>
> measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force
>
> attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Properties of Liquids
By the end of this section, you will be able to:

- Distinguish between adhesive and cohesive forces
- Define viscosity, surface tension, and capillary rise
- Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The **viscosity** of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in [link], have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).
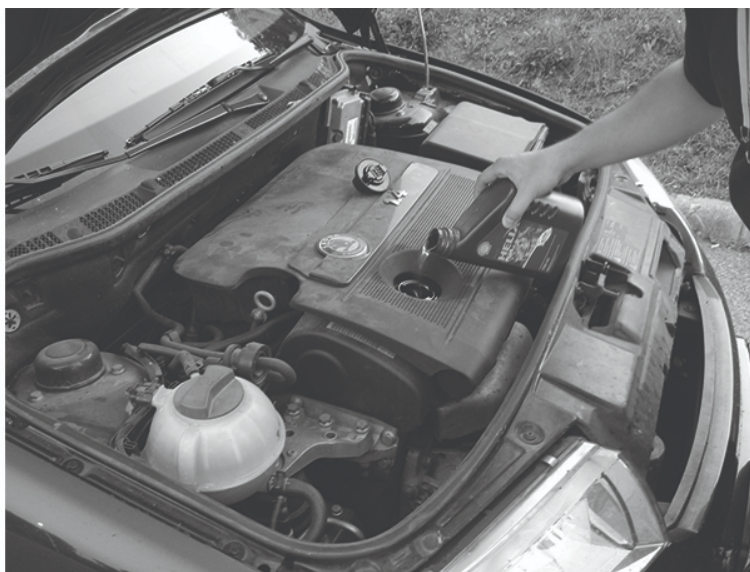
(a)   (b)

(a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As [link] shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Viscosities of Common Substances at 25 °C		
Substance	**Formula**	**Viscosity (mPa·s)**
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of **cohesive forces**. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces

within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface— that is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in [link], because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.
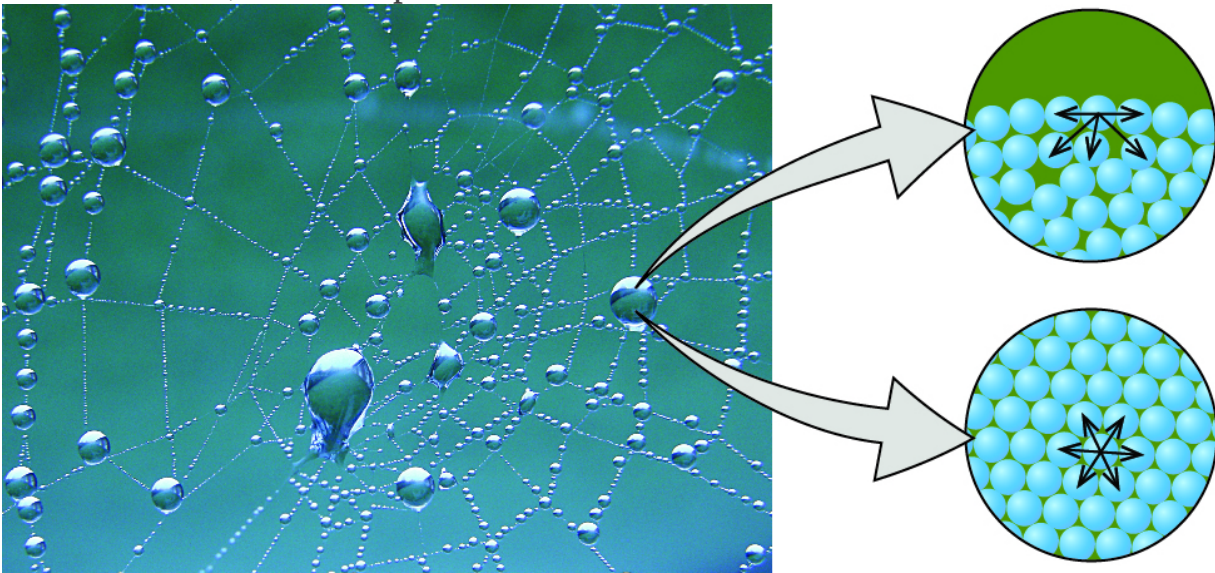
Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by "OliBac"/Flickr)

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in [link]. Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface

of water represents a relatively "tough skin" that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in [link], even though they are denser than water, move on its surface because they are supported by the surface tension.

Surface Tensions of Common Substances at 25 °C		
Substance	**Formula**	**Surface Tension (mN/m)**
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99
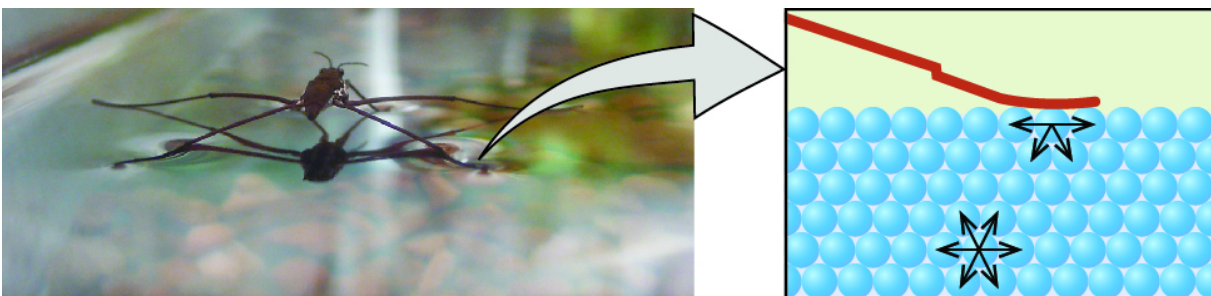
Surface tension (right) prevents this insect, a "water strider," from sinking into the water.

The IMFs of attraction between two *different* molecules are called **adhesive forces**. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not "wet" the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop ([link]).
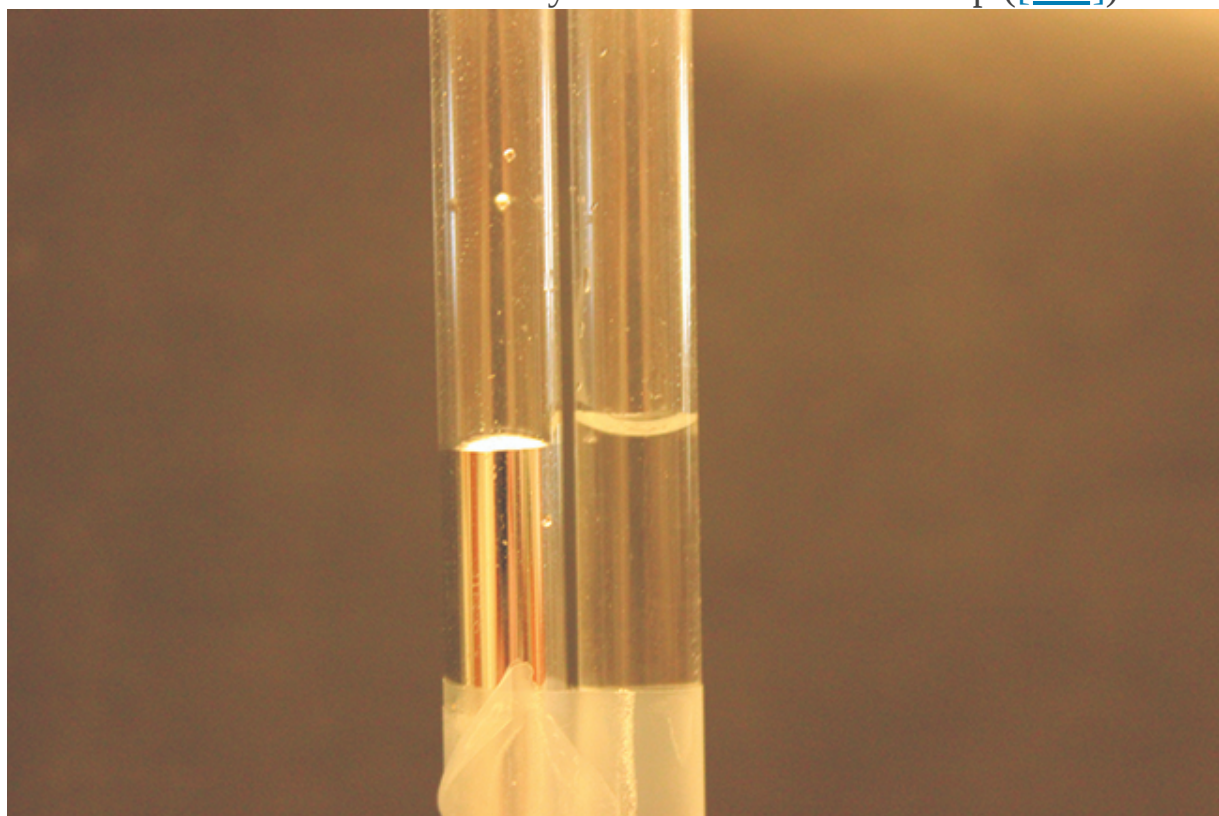
Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

If you place one end of a paper towel in spilled wine, as shown in [link], the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of **capillary action**—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.
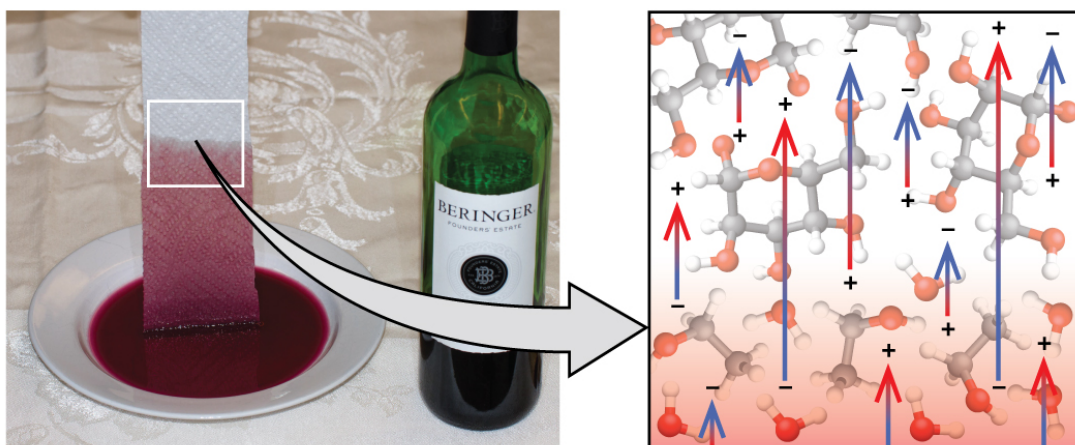
Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the −OH groups on the towel's cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many −OH groups. Water molecules are attracted to these −OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in [link]. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.
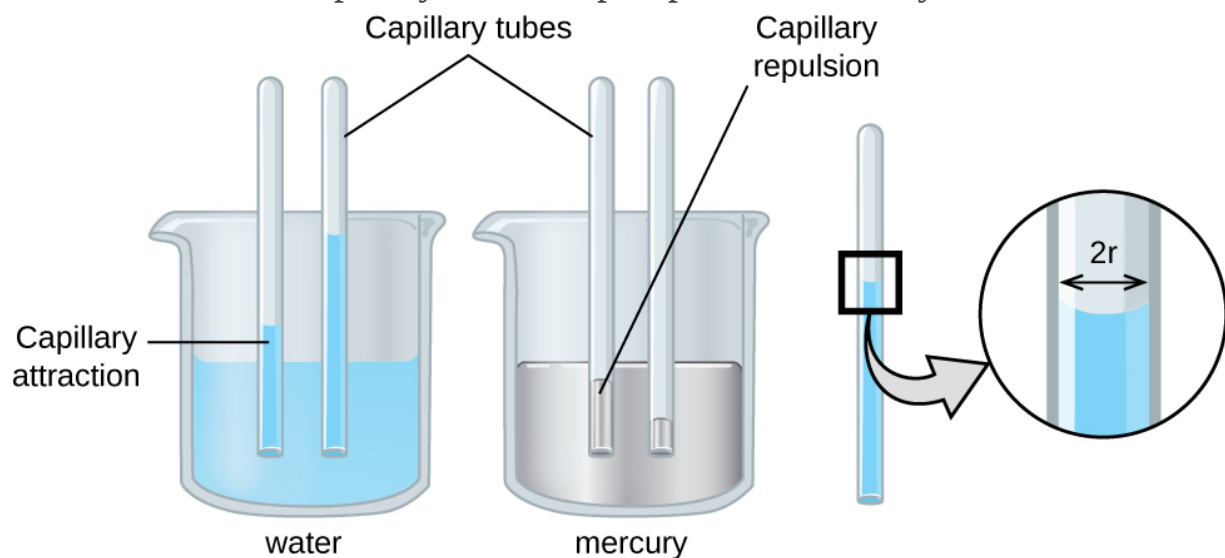
Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to

the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

Note:
Biomedical Applications of Capillary Action
Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in [link]. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.

Blood is collected for medical

analysis by capillary action, which
draws blood into a small diameter
glass tube. (credit: modification of
work by Centers for Disease
Control and Prevention)

Key Concepts and Summary

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid's viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

Chemistry End of Chapter Exercises

Exercise:

Problem:

The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration.

Rank the motor oils in order of increasing viscosity, and explain your reasoning:

Oil viscosity (SAE)
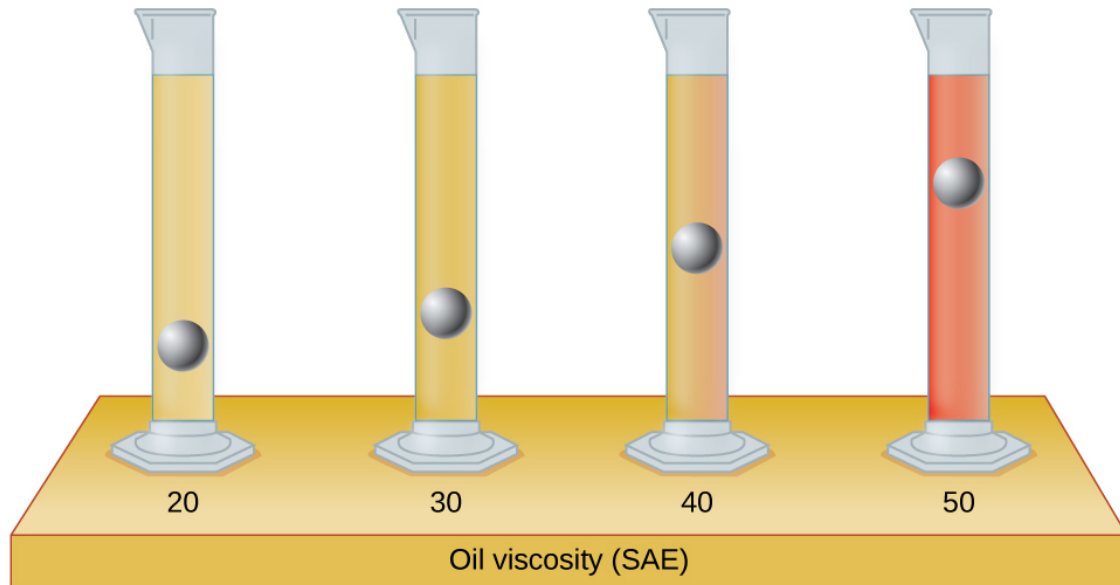
Exercise:

Problem:

Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible:
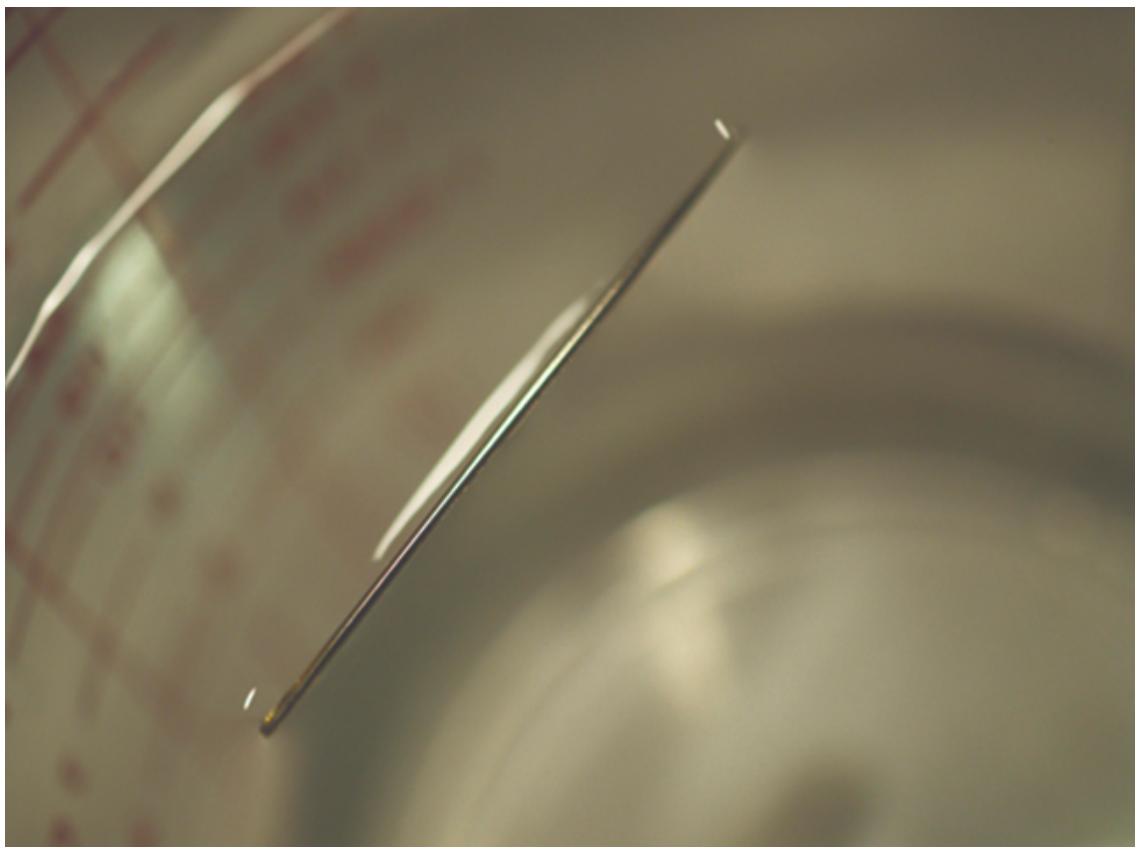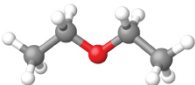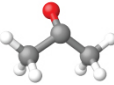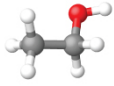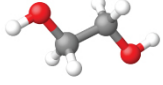
(credit: Cory Zanker)

Solution:

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of "skin" at its surface. This skin can support a bug or paper clip if gently placed on the water.

Exercise:

Problem:

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

(a) Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.

(b) Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

Exercise:

Problem:

You may have heard someone use the figure of speech "slower than molasses in winter" to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

Solution:

Temperature has an effect on intermolecular forces: the higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid; the lower the temperature, the lesser the intermolecular forces are overcome, and so the less viscous the liquid.

Exercise:

Problem:

The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

(a) As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

(b) As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

Solution:

(a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

Glossary

adhesive force
> force of attraction between molecules of different chemical identities

capillary action
> flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

cohesive force
> force of attraction between identical molecules

surface tension
> energy required to increase the area, or length, of a liquid surface by a given amount

viscosity
> measure of a liquid's resistance to flow

Phase Transitions
By the end of this section, you will be able to:

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures and intermolecular attractive forces
- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called **condensation**. When the rate of condensation becomes equal to the rate of **vaporization**, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a **dynamic equilibrium**, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's **vapor pressure** (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in [link], and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.
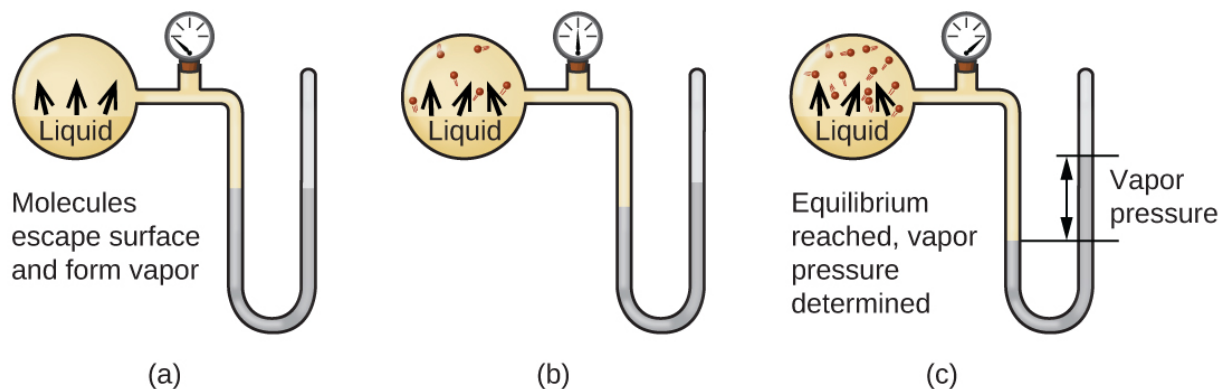
In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

Example:
Explaining Vapor Pressure in Terms of IMFs
Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:
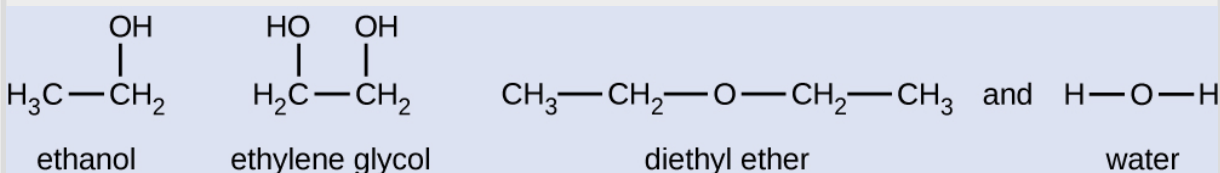
Solution
Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two −OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure the lowest.

Check Your Learning
At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Note:
Answer:
All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase,

which means that the vapor pressures decrease as observed:
$P_{methanol} > P_{ethanol} > P_{propanol} > P_{butanol}$.

As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in [link]. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.
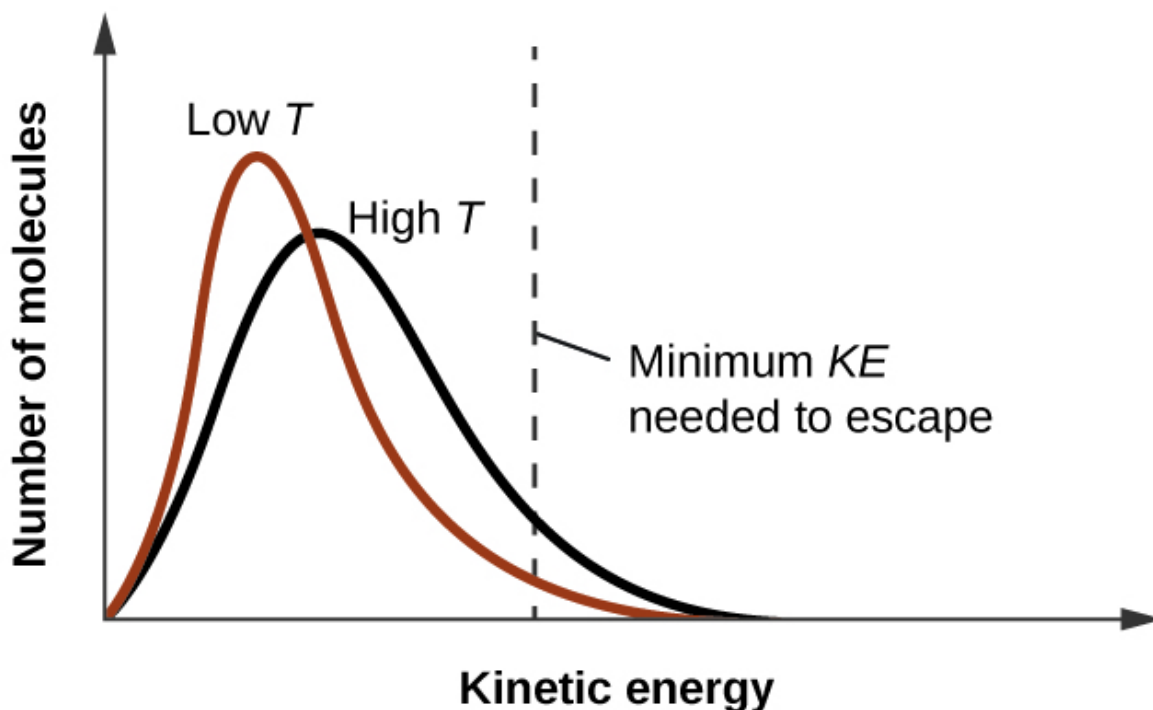
Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The **boiling point** of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The **normal boiling point** of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). [link] shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.
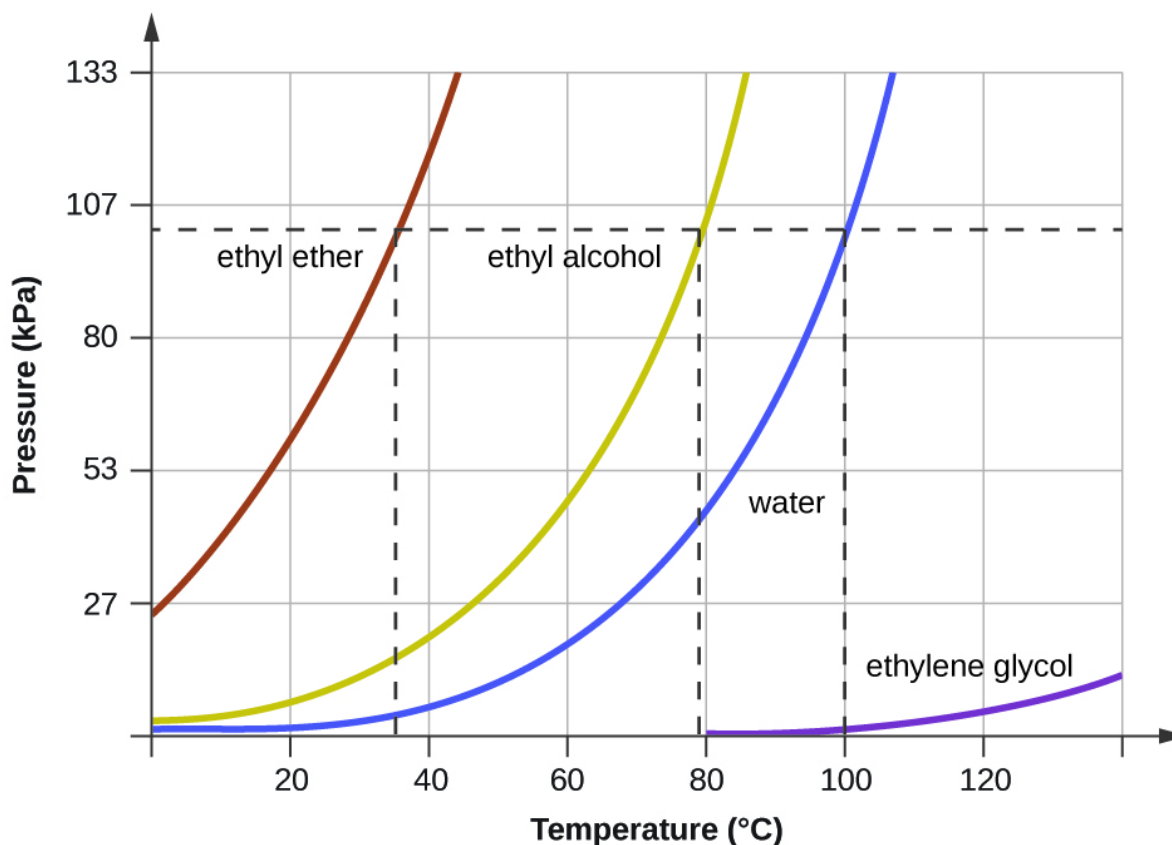
The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. For example, the vaporization of water at standard temperature is represented by:
Equation:

$$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g) \qquad \Delta H_{\text{vap}} = 44.01 \text{ kJ/mol}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

Equation:

$$H_2O(g) \longrightarrow H_2O(l) \qquad \Delta H_{con} = -\Delta H_{vap} = -44.01 \text{ kJ/mol}$$

Example:

Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat ([link]). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at $T = 37$ °C (normal body temperature); $\Delta H_{vap} = 43.46$ kJ/mol at 37 °C.

Evaporation of sweat helps cool the body. (credit: "Kullez"/Flickr)

Solution

We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:
Equation:

$$1.5 \, \cancel{\text{L}} \times \frac{1000 \, \cancel{\text{g}}}{1 \, \cancel{\text{L}}} \times \frac{1 \, \cancel{\text{mol}}}{18 \, \cancel{\text{g}}} \times \frac{43.46 \, \text{kJ}}{1 \, \cancel{\text{mol}}} = 3.6 \times 10^3 \, \text{kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.
Check Your Learning
How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3, at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Note:
Answer:
28 kJ

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or **melting**. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid ([link]).

(a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott)

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of melting and **freezing** occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the **melting point** of the solid or the **freezing point** of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

Equation:

$$H_2O(s) \longrightarrow H_2O(l) \qquad\qquad \Delta H_{fus} = 6.01 \text{ kJ/mol}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

Equation:

$$H_2O(l) \longrightarrow H_2O(s) \qquad \Delta H_{frz} = -\Delta H_{fus} = -6.01 \, kJ/mol$$

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms ([link]). The reverse of sublimation is called **deposition**, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.
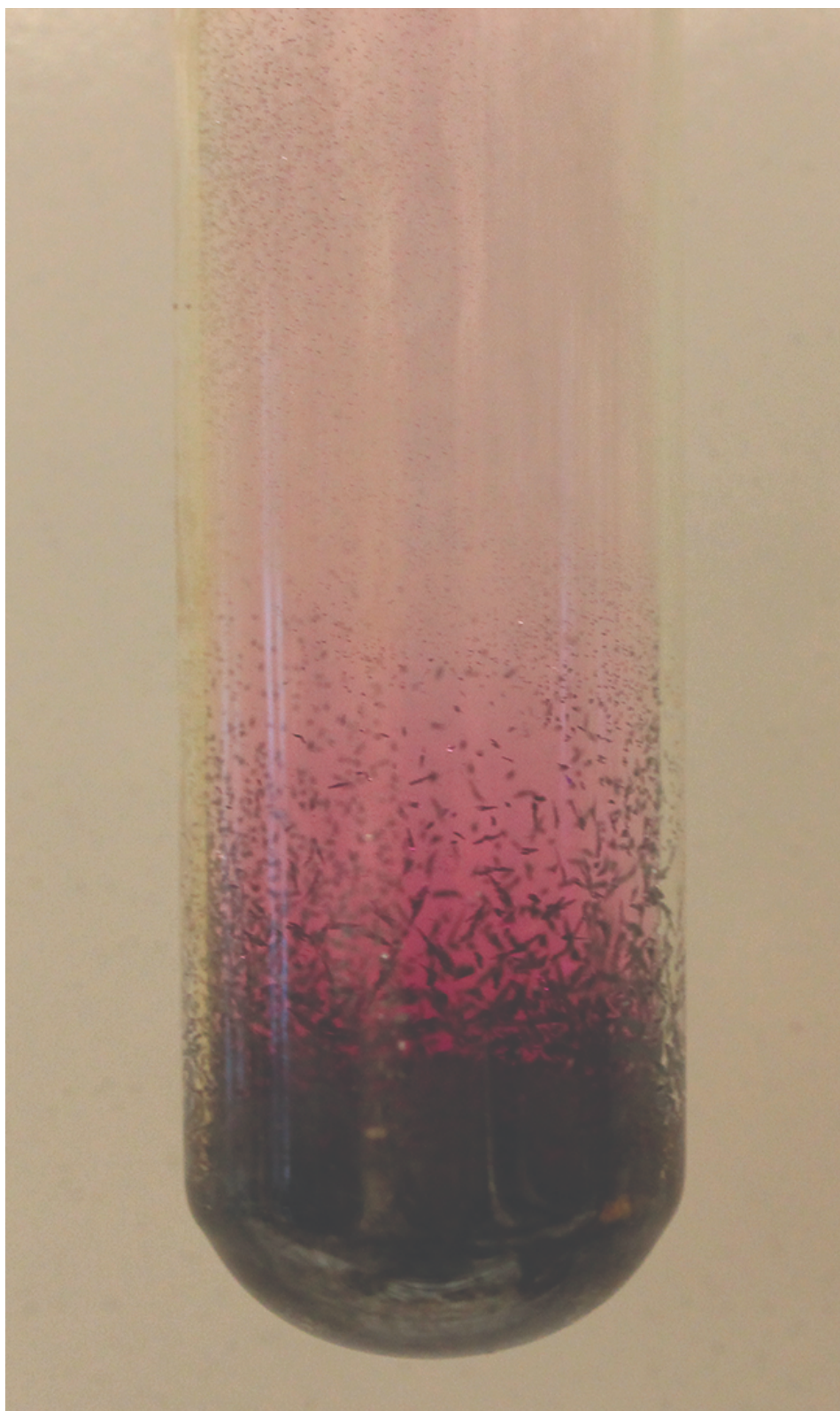
Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub}, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

Equation:

$$CO_2(s) \longrightarrow CO_2(g) \qquad\qquad \Delta H_{sub} = 26.1 \text{ kJ/mol}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

Equation:

$$CO_2(g) \longrightarrow CO_2(s) \qquad\qquad \Delta H_{dep} = -\Delta H_{sub} = -26.1 \text{ kJ/mol}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law. Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in [link]. For example:

Equation:

$$
\begin{aligned}
\text{solid} &\longrightarrow \text{liquid} & \Delta H_{fus} \\
\text{liquid} &\longrightarrow \text{gas} & \Delta H_{vap} \\
\text{solid} &\longrightarrow \text{gas} & \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}
\end{aligned}
$$
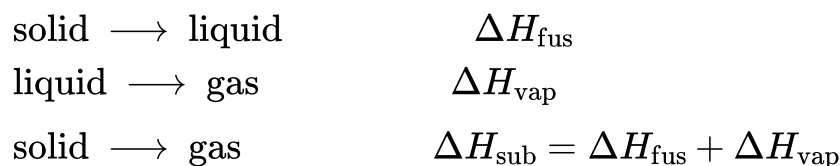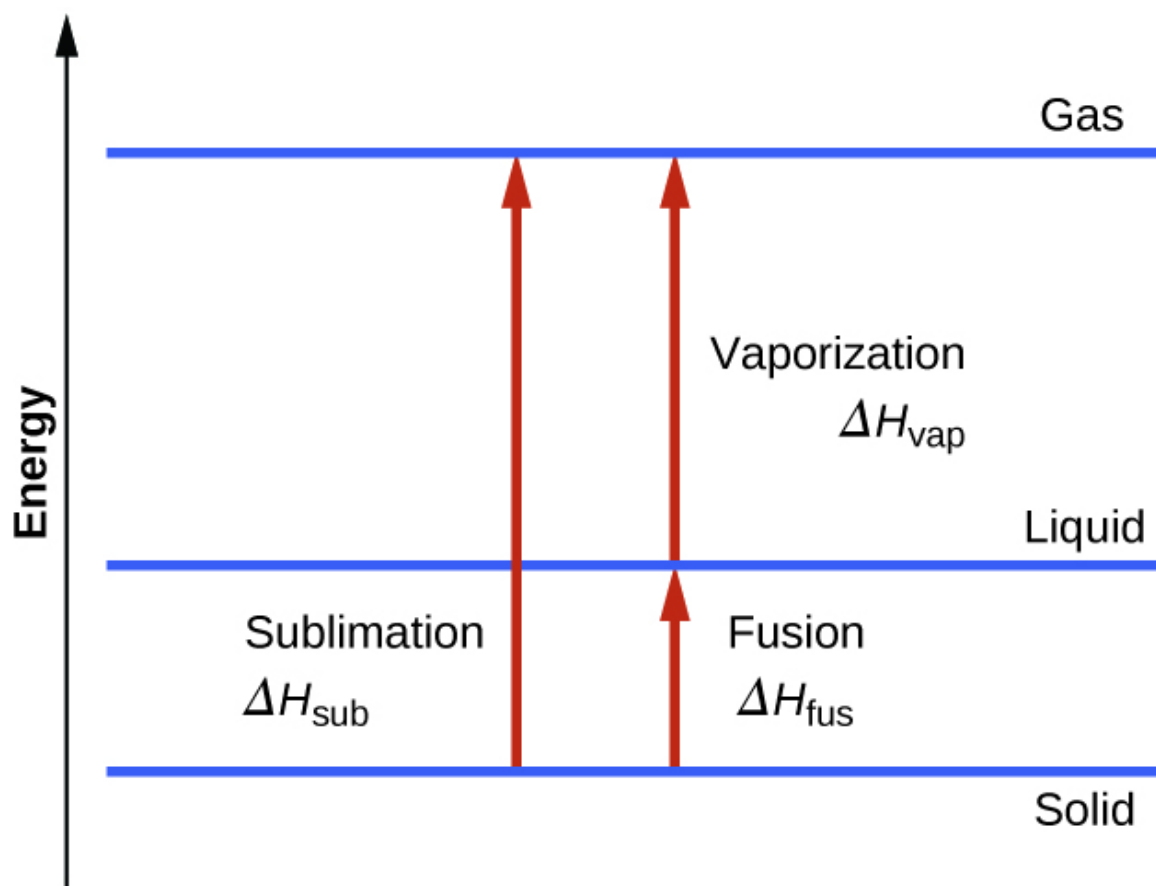
For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.

Heating and Cooling Curves

In the chapter on thermochemistry, the relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, was introduced:

Equation:

$$q = mc\Delta T$$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance being heated or cooled reaches a temperature corresponding to one of its

phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. [link] shows a typical heating curve.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.
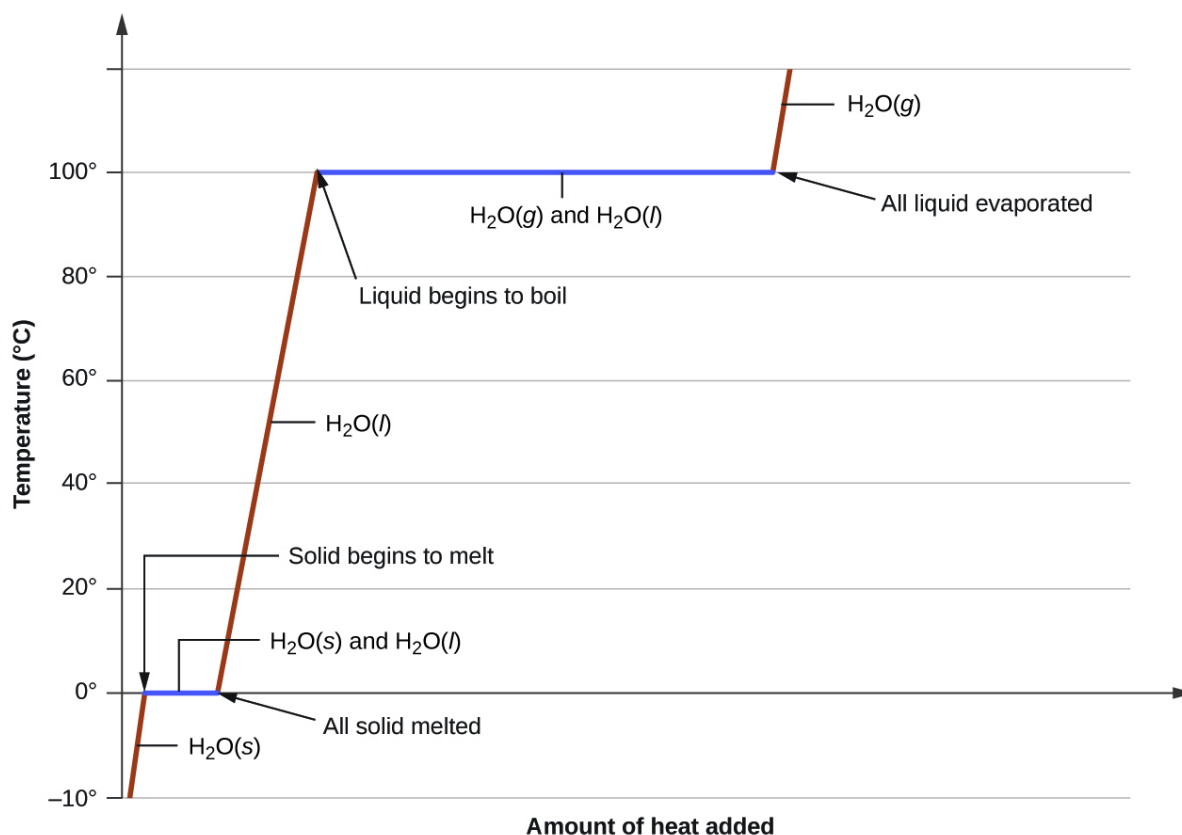
A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the

curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

Example:
Total Heat Needed to Change Temperature and Phase for a Substance
How much heat is required to convert 135 g of ice at −15 °C into water vapor at 120 °C?
Solution
The transition described involves the following steps:

1. Heat ice from −15 °C to 0 °C
2. Melt ice
3. Heat water from 0 °C to 100 °C
4. Boil water
5. Heat steam from 100 °C to 120 °C

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = m \times c \times \Delta T$ (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by $q = n \times \Delta H$.
Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:
Equation:

$$q_{\text{total}} = (m{\cdot}c{\cdot}\Delta T)_{\text{ice}} + n{\cdot}\Delta H_{\text{fus}} + (m{\cdot}c{\cdot}\Delta T)_{\text{water}} + n{\cdot}\Delta H_{\text{vap}} + (m{\cdot}c{\cdot}\Delta T)_{\text{steam}}$$

Equation:

$$= (135 \text{ g}{\cdot}2.09 \text{ J/g}{\cdot}°\text{C}{\cdot}15\,°\text{C}) + \;\; 135{\cdot}\tfrac{1\,\text{mol}}{18.02\,\text{g}}{\cdot}6.01 \text{ kJ/mol}$$

$$+ (135 \text{ g}{\cdot}4.18 \text{ J/g}{\cdot}°\text{C}{\cdot}100\,°\text{C}) + \;\; 135 \text{ g}{\cdot}\tfrac{1\,\text{mol}}{18.02\,\text{g}}{\cdot}40.67 \text{ kJ/mol}$$

$$+ (135 \text{ g}{\cdot}1.84 \text{ J/g}{\cdot}°\text{C}{\cdot}20\,°\text{C})$$

$$= 4230 \text{ J} + 45.0 \text{ kJ} + 56{,}500 \text{ J} + 305 \text{ kJ} + 4970 \text{ J}$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

Key Concepts and Summary

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

Chemistry End of Chapter Exercises

Exercise:

  Problem:

  Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

Exercise:

Problem:

Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

Solution:

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

Exercise:

Problem:

Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

Solution:

We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

Exercise:

Problem:

Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

Exercise:

Problem:

What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

Solution:

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

Exercise:

Problem:

What is the relationship between the intermolecular forces in a solid and its melting temperature?

Exercise:

Problem:

Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

Solution:

As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

Exercise:

Problem:

When is the boiling point of a liquid equal to its normal boiling point?

Solution:

When the pressure of gas above the liquid is exactly 1 atm

Exercise:

Problem: How does the boiling of a liquid differ from its evaporation?

Exercise:

Problem:

Use the information in [link] to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

Solution:

approximately 95 °C

Exercise:

Problem:

A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

Exercise:

Problem: Explain the following observations:

(a) It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).

(b) Perspiring is a mechanism for cooling the body.

Solution:

(a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

Exercise:

Problem:

The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

Exercise:

Problem:

Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though the type of IMF (dispersion) is the same.

Solution:

Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

Exercise:

Problem:

Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

Exercise:

Problem:

The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or −8.4 kJ/mol? Discuss the plausibility of each of these answers.

Solution:

The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of −8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

Exercise:

Problem:

Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

Solution:

The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

Exercise:

Problem:

Which contains the compounds listed correctly in order of increasing boiling points?

(a) $N_2 < CS_2 < H_2O < KCl$

(b) $H_2O < N_2 < CS_2 < KCl$

(c) $N_2 < KCl < CS_2 < H_2O$

(d) $CS_2 < N_2 < KCl < H_2O$

(e) $KCl < H_2O < CS_2 < N_2$

Exercise:

Problem:

How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

Solution:

1130 kJ

Exercise:

Problem:

Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a ΔH fusion = 9.37 kJ/mol.

(a) How much energy is required to melt 263.1 g $TiCl_4$?

(b) For $TiCl_4$, which will likely have the larger magnitude: ΔH fusion or ΔH vaporization? Explain your reasoning.

Solution:

(a) 13.0 kJ; (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

Glossary

boiling point
    temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Clausius-Clapeyron equation
    mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

condensation
    change from a gaseous to a liquid state

deposition
    change from a gaseous state directly to a solid state

dynamic equilibrium
    state of a system in which reciprocal processes are occurring at equal rates

freezing
    change from a liquid state to a solid state

freezing point
    temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

melting
    change from a solid state to a liquid state

melting point
    temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

normal boiling point
    temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

sublimation
    change from solid state directly to gaseous state

vapor pressure

(also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization
change from liquid state to gaseous state

Phase Diagrams
By the end of this section, you will be able to:

- Explain the construction and use of a typical phase diagram
- Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions resulting from changes in these properties
- Describe the supercritical fluid phase of matter

In the previous module, the variation of a liquid's equilibrium vapor pressure with temperature was described. Considering the definition of boiling point, plots of vapor pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A **phase diagram** combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in [link].
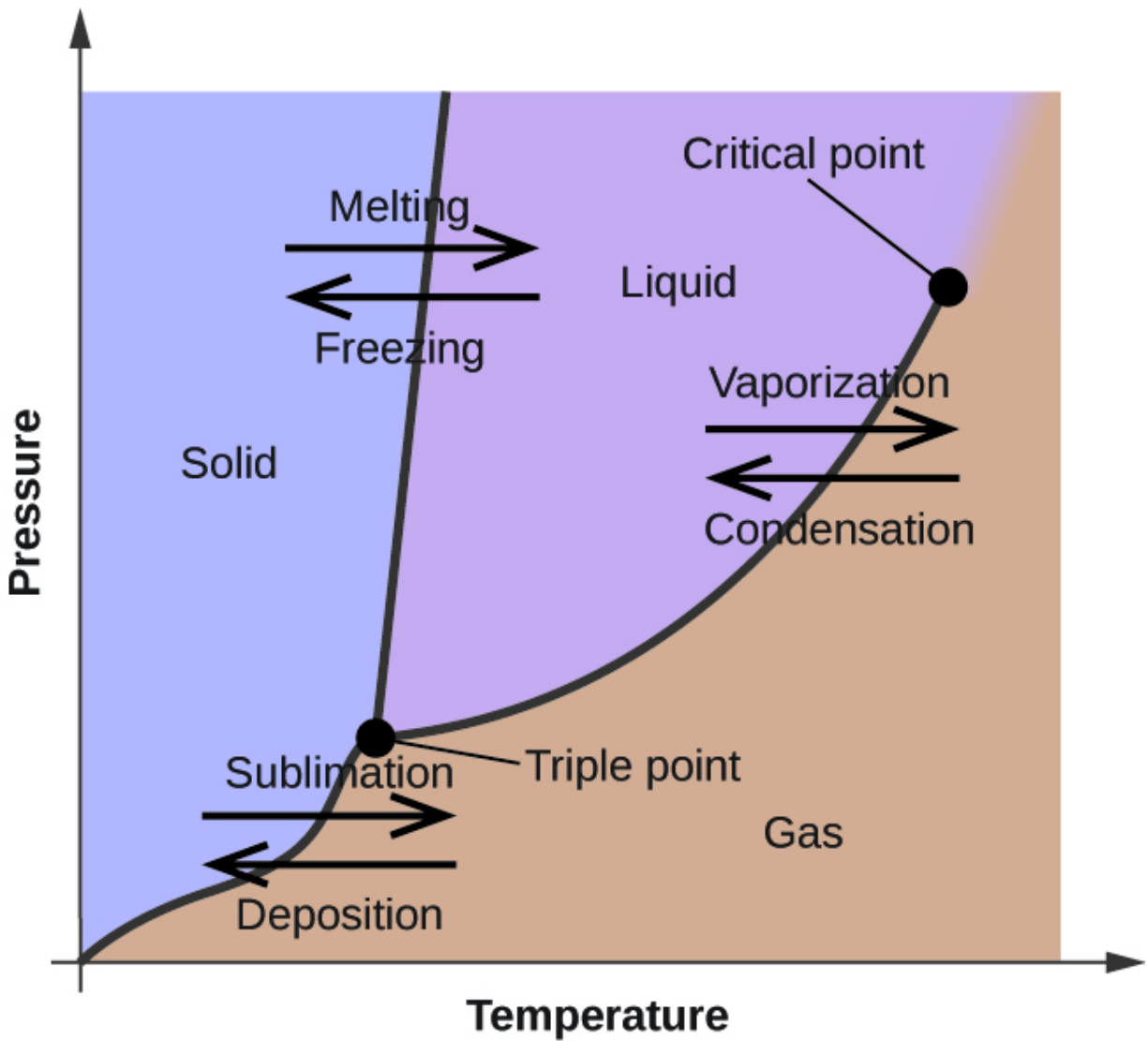
The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram.

To illustrate the utility of these plots, consider the phase diagram for water shown in [link].
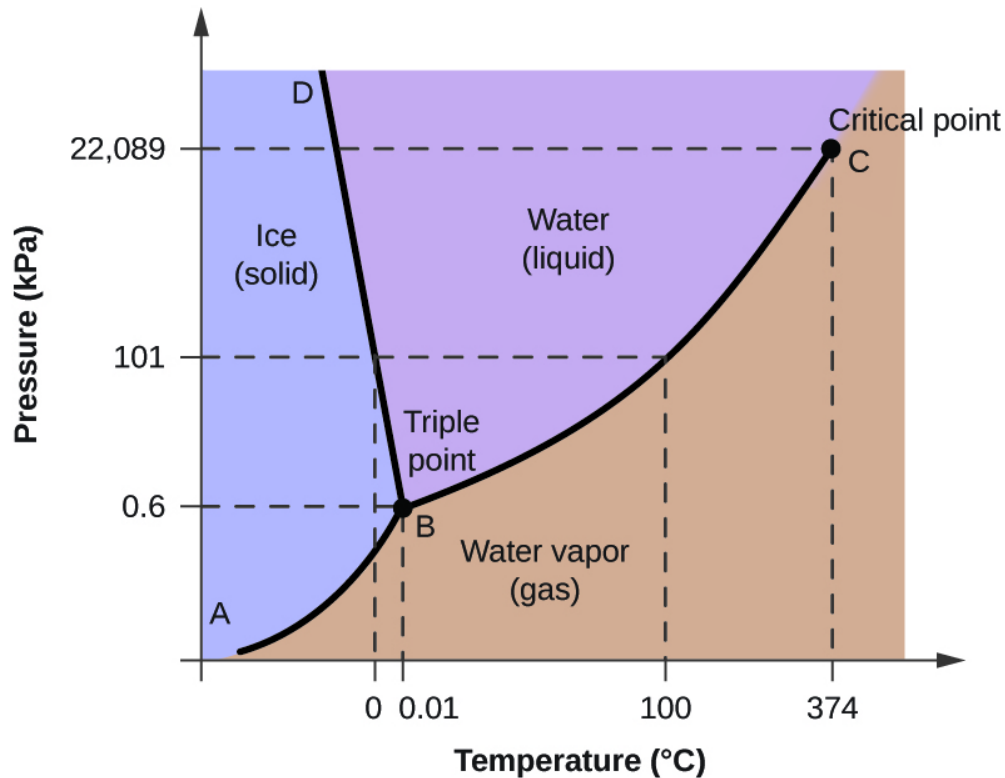
The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties.

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of −10 °C correspond to the region of the diagram labeled "ice." Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50 °C correspond to the "water" region—here, water exists only as a liquid. At 25 kPa and 200 °C, water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in [link] is the plot of vapor pressure versus temperature as described in the previous module of this chapter. This "liquid-vapor" curve

separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapor curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapor curve, labeled AB in [link], indicates the temperatures and pressures at which ice and water vapor are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in [link], we would see that ice has a vapor pressure of about 0.20 kPa at −10 °C. Thus, if we place a frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the "freeze-drying" process often used to preserve foods, such as the ice cream shown in [link].

Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: "Iwao"/Flickr)

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behavior is partly responsible for the movement of glaciers, like the one shown in [link]. The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.

The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: NASA)

The point of intersection of all three curves is labeled B in [link]. At the pressure and temperature represented by this point, all three phases of water coexist in equilibrium. This temperature-pressure data pair is called the **triple point**. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.

Example:
Determining the State of Water
Using the phase diagram for water given in [link], determine the state of water at the following temperatures and pressures:

(a) −10 °C and 50 kPa
(b) 25 °C and 90 kPa
(c) 50 °C and 40 kPa
(d) 80 °C and 5 kPa
(e) −10 °C and 0.3 kPa
(f) 50 °C and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure given are as follows: (a) solid; (b) liquid; (c) liquid; (d) gas; (e) solid; (f) gas.

Check Your Learning

What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? If the pressure is held at 50 kPa?

Note:

Answer:

At 0.3 kPa: s $\longrightarrow$ g at −58 °C. At 50 kPa: s $\longrightarrow$ l at 0 °C, l $\longrightarrow$ g at 78 °C

Consider the phase diagram for carbon dioxide shown in [link] as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimes to yield gaseous CO_2. Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.
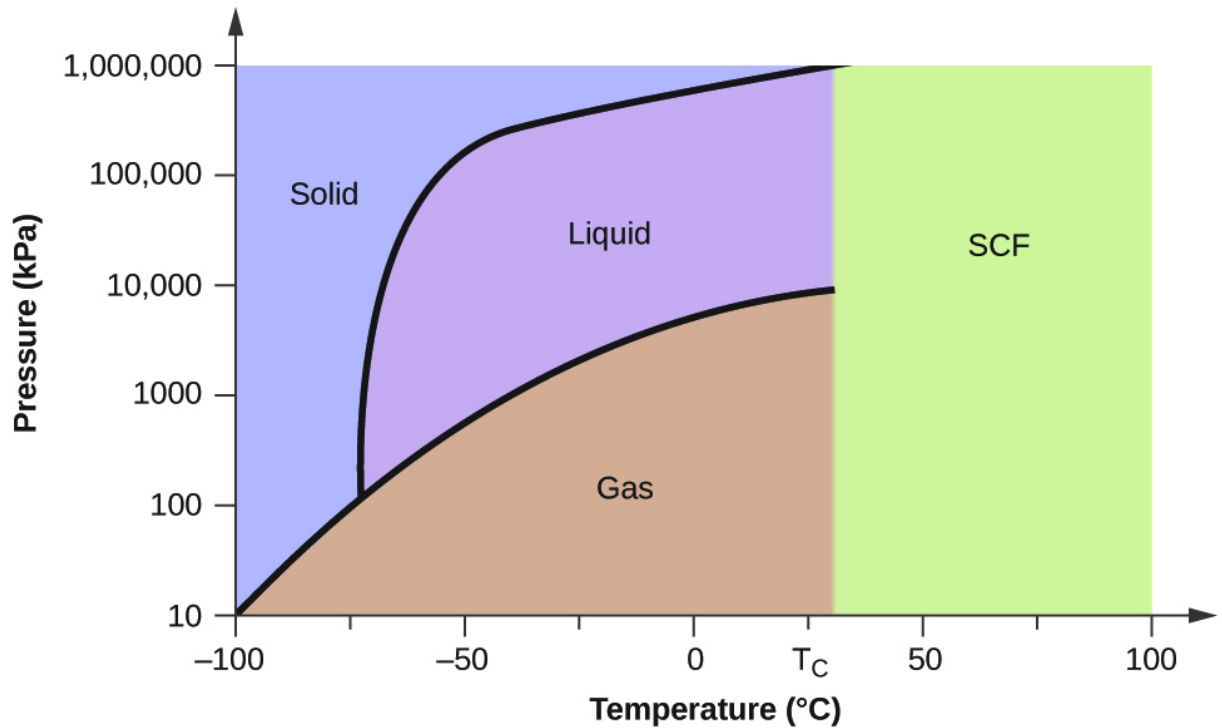
The pressure and temperature axes on this phase diagram of carbon dioxide are not drawn to constant scale in order to illustrate several important properties.

Example:
Determining the State of Carbon Dioxide
Using the phase diagram for carbon dioxide shown in [link], determine the state of CO_2 at the following temperatures and pressures:
(a) −30 °C and 2000 kPa
(b) −60 °C and 1000 kPa
(c) −60 °C and 100 kPa
(d) 20 °C and 1500 kPa
(e) 0 °C and 100 kPa
(f) 20 °C and 100 kPa
Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO_2 at each temperature and pressure given are as follows: (a) liquid; (b) solid; (c) gas; (d) liquid; (e) gas; (f) gas.

Check Your Learning

Determine the phase changes carbon dioxide undergoes when its temperature is varied, thus holding its pressure constant at 1500 kPa? At 500 kPa? At what approximate temperatures do these phase changes occur?

Note:
Answer:

at 1500 kPa: s $\longrightarrow$ l at −45 °C, l $\longrightarrow$ g at −10 °C;

at 500 kPa: s $\longrightarrow$ g at −58 °C

Key Concepts and Summary

The temperature and pressure conditions at which a substance exists in solid, liquid, and gaseous states are summarized in a phase diagram for that substance. Phase diagrams are combined plots of three pressure-temperature equilibrium curves: solid-liquid, liquid-gas, and solid-gas. These curves represent the relationships between phase-transition temperatures and pressures. The point of intersection of all three curves represents the substance's triple point—the temperature and pressure at which all three phases are in equilibrium. At pressures below the triple point, a substance cannot exist in the liquid state, regardless of its temperature. The terminus of the liquid-gas curve represents the substance's critical point, the pressure and temperature above which a liquid phase cannot exist.

Chemistry End of Chapter Exercises

Exercise:

Problem:

From the phase diagram for water ([link]), determine the state of water at:

(a) 35 °C and 85 kPa

(b) −15 °C and 40 kPa

(c) −15 °C and 0.1 kPa

(d) 75 °C and 3 kPa

(e) 40 °C and 0.1 kPa

(f) 60 °C and 50 kPa

Exercise:

Problem:

What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C?

Solution:

At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At −40 °C, water goes from a gas to a solid as the pressure increases above very low values.

Exercise:

Problem:

Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

Exercise:

Problem:

From the phase diagram for carbon dioxide in [link], determine the state of CO_2 at:

(a) 20 °C and 1000 kPa

(b) 10 °C and 2000 kPa

(c) 10 °C and 100 kPa

(d) −40 °C and 500 kPa

(e) −80 °C and 1500 kPa

(f) −80 °C and 10 kPa

Solution:

(a) liquid; (b) solid; (c) gas; (d) gas; (e) gas; (f) gas

Exercise:

Problem:

Determine the phase changes that carbon dioxide undergoes as the pressure changes if the temperature is held at −50 °C? If the temperature is held at −40 °C? At 20 °C? (See the phase diagram in [link].)

Exercise:

  Problem:

  Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See [link] for the phase diagram.)

Exercise:

  Problem:

  Some people choose to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

  Solution:

  Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

Exercise:

  Problem:

  Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the phase diagram:
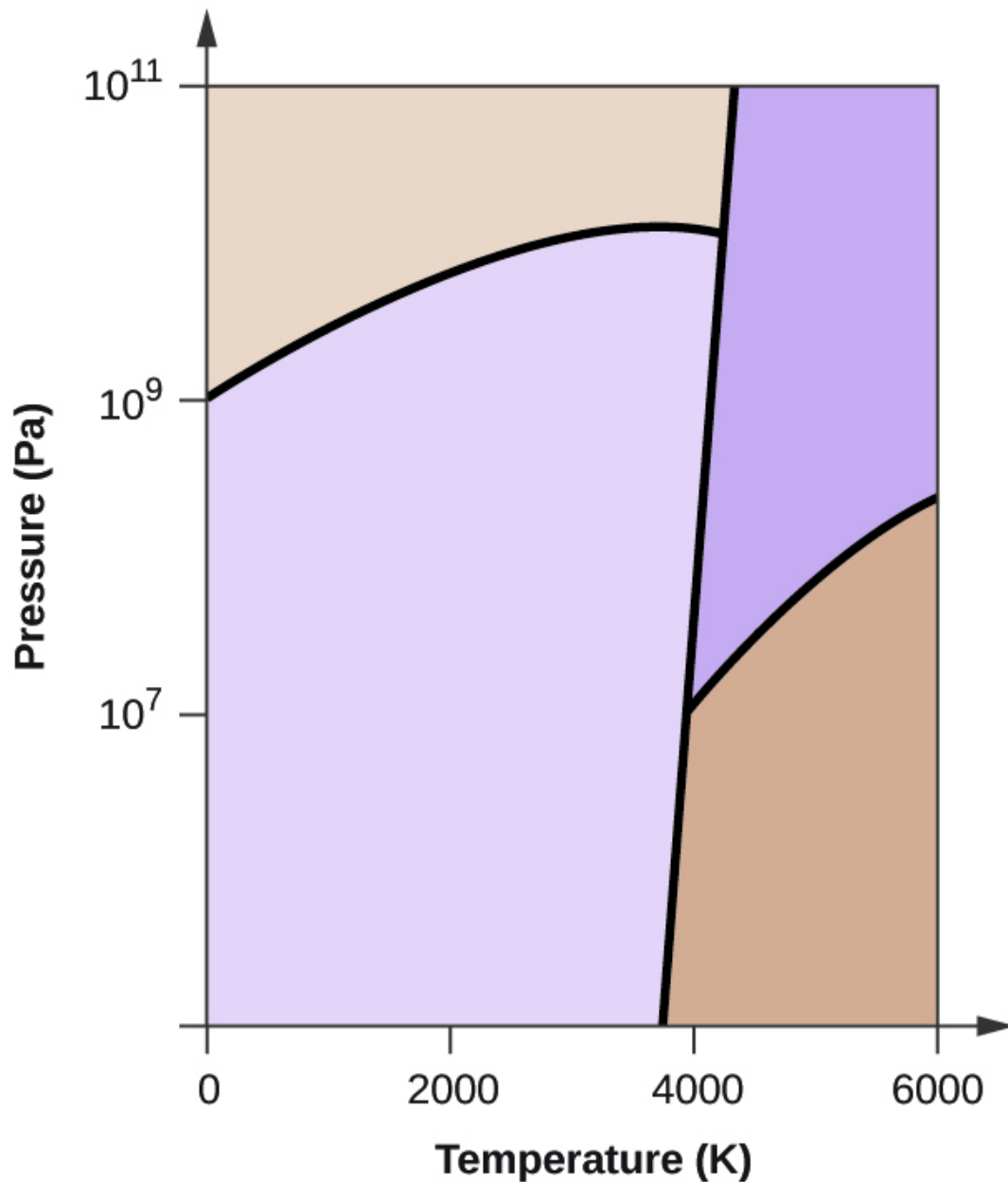
(a) On the phase diagram, label the gas and liquid regions.

(b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.

(c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.

(d) Circle each triple point on the phase diagram.

(e) In what phase does carbon exist at 5000 K and 10^8 Pa?

(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any?

Solution:

(a)
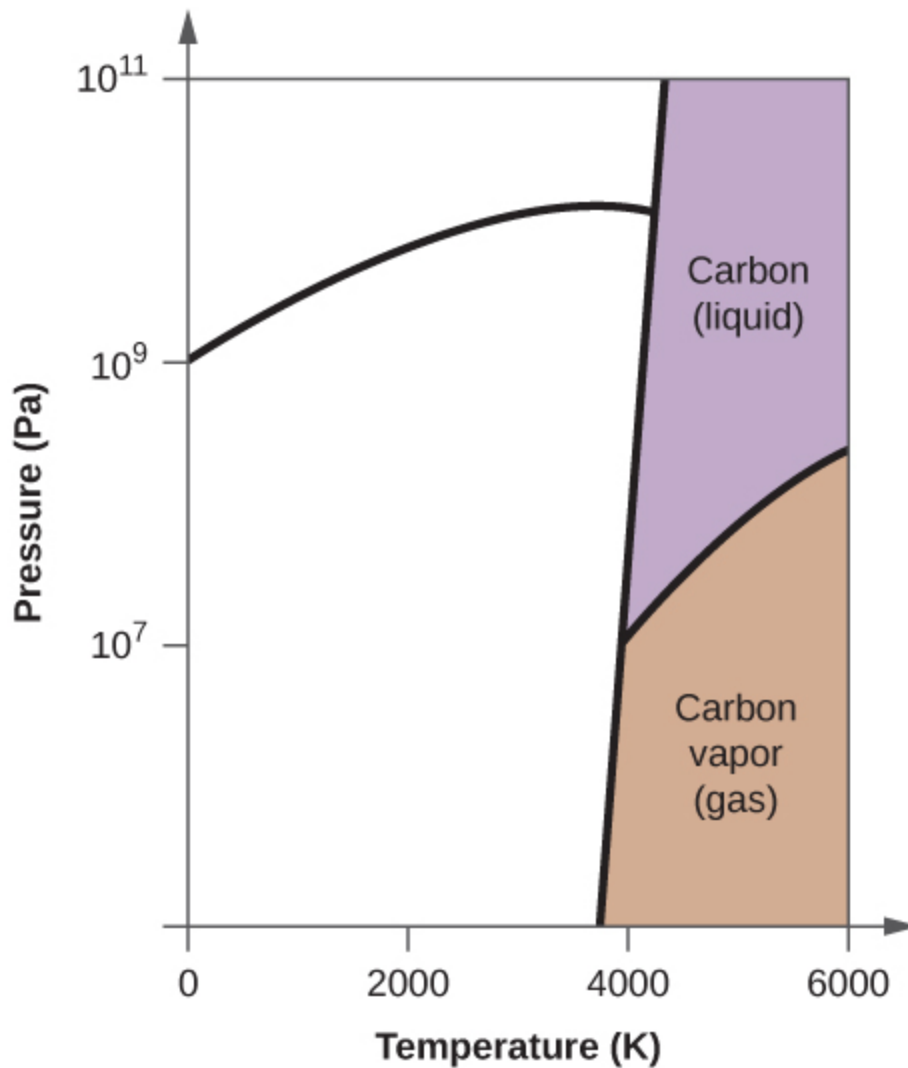
(b)
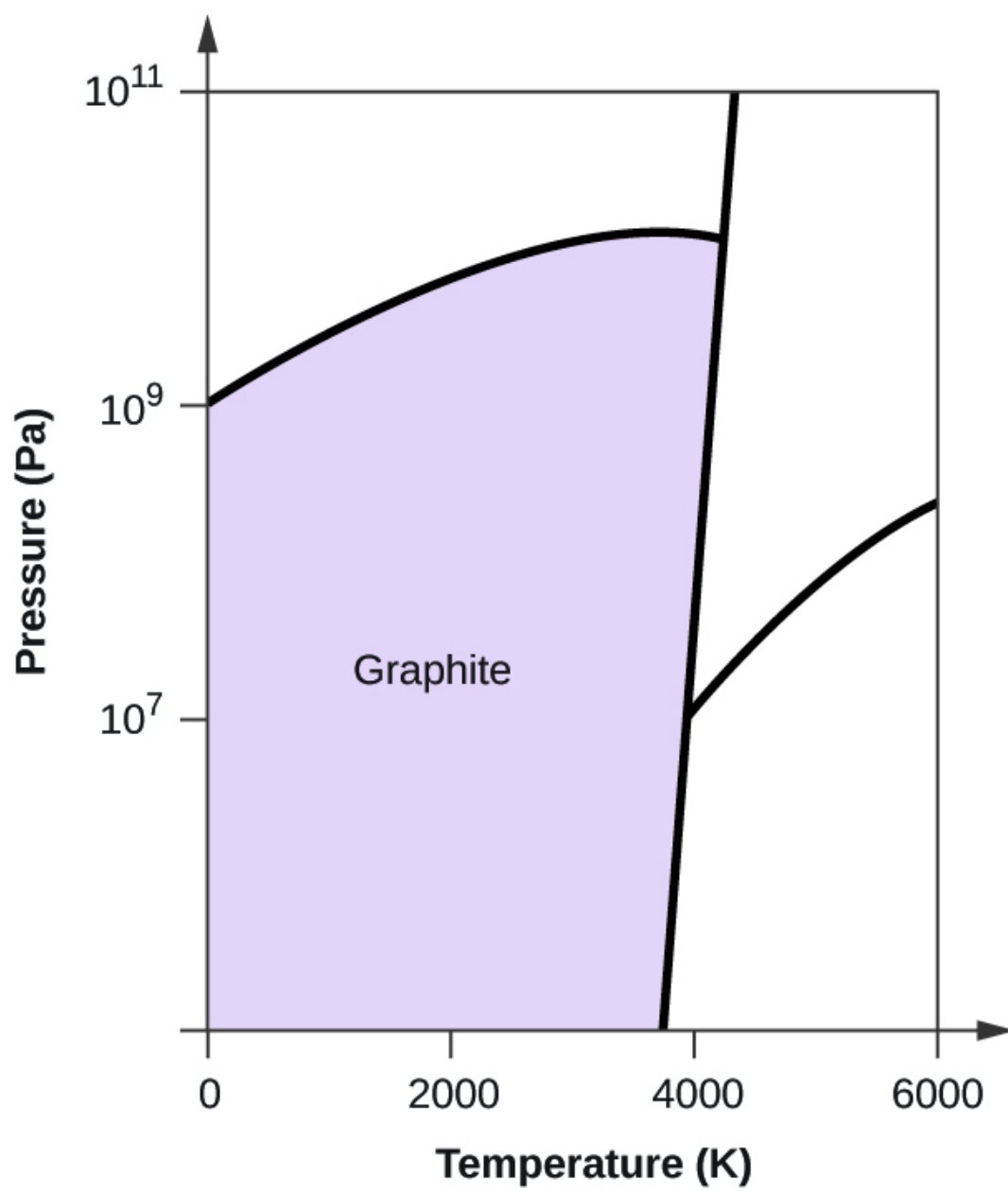
(c)
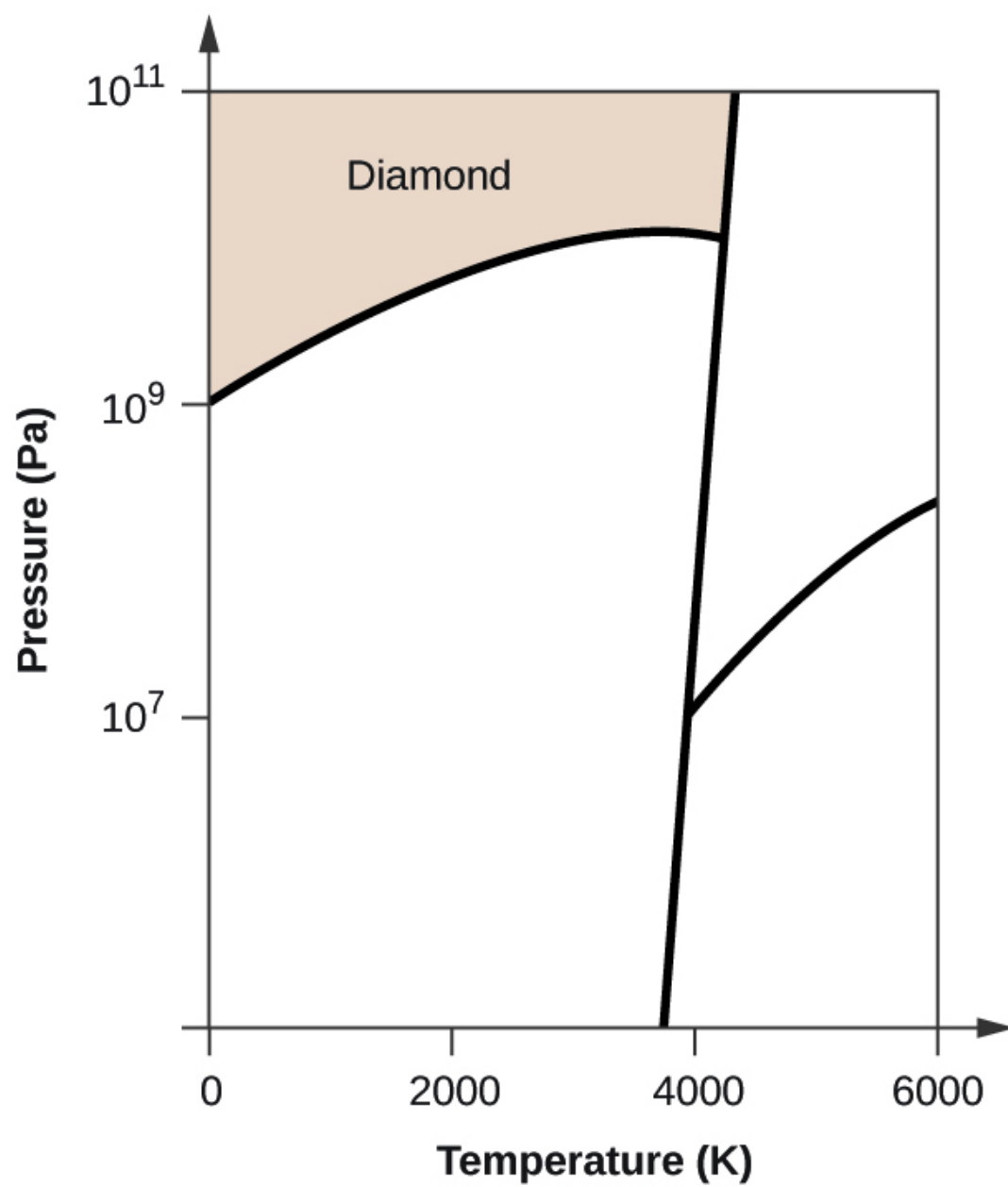
(d)
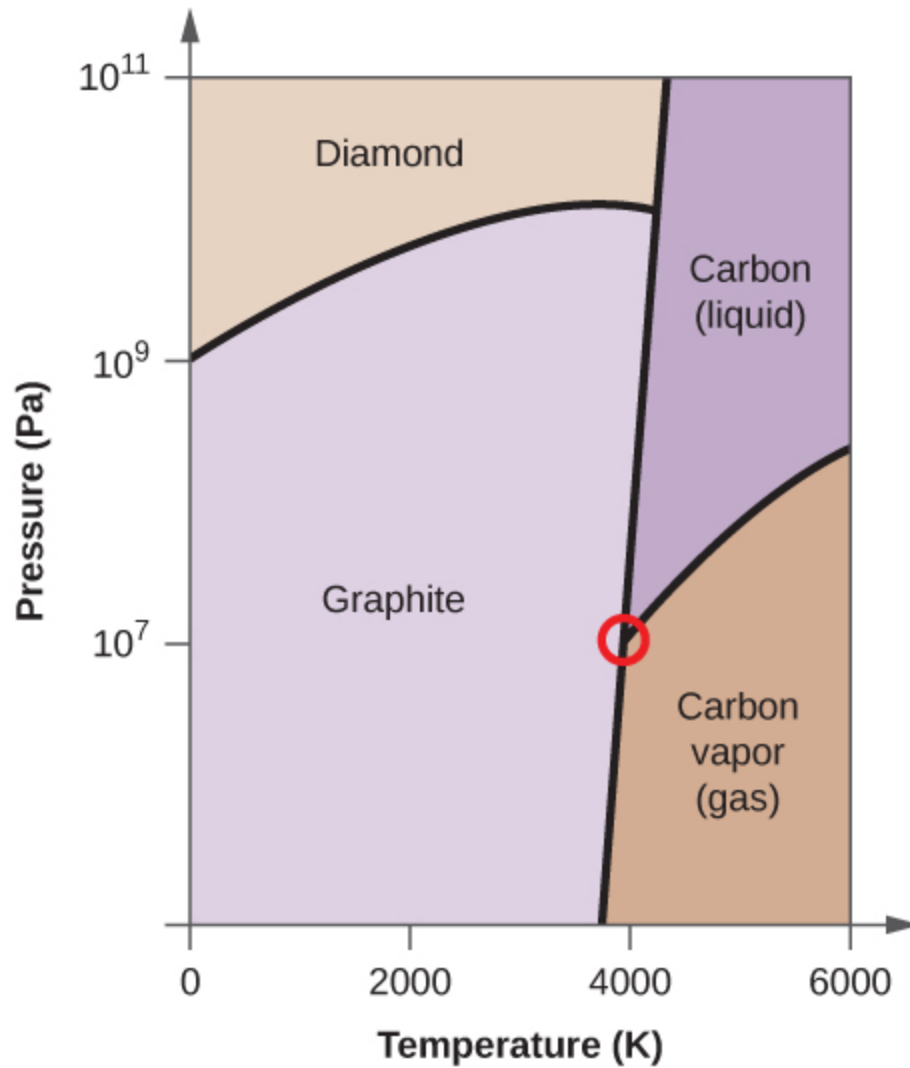
(e) liquid phase (f) sublimation

Glossary

critical point
> temperature and pressure above which a gas cannot be condensed into a liquid

phase diagram
> pressure-temperature graph summarizing conditions under which the phases of a substance can exist

supercritical fluid
: substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

triple point
: temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

The Solid State of Matter
By the end of this section, you will be able to:

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form **crystalline solids**, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called **amorphous solids** or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged ([link]).
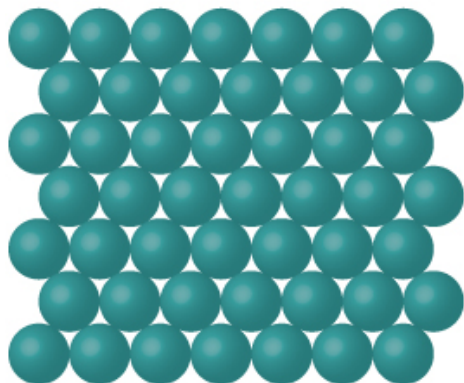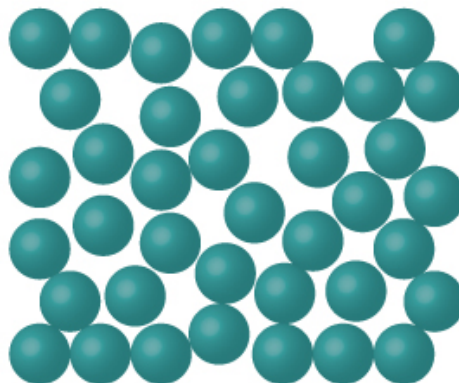
Crystalline   Amorphous

The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as boron oxide (shown in [link]), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.
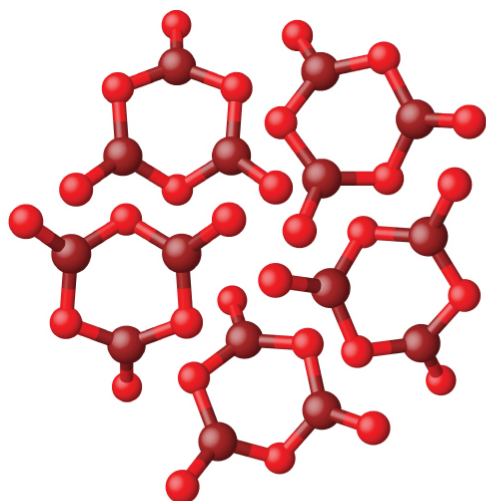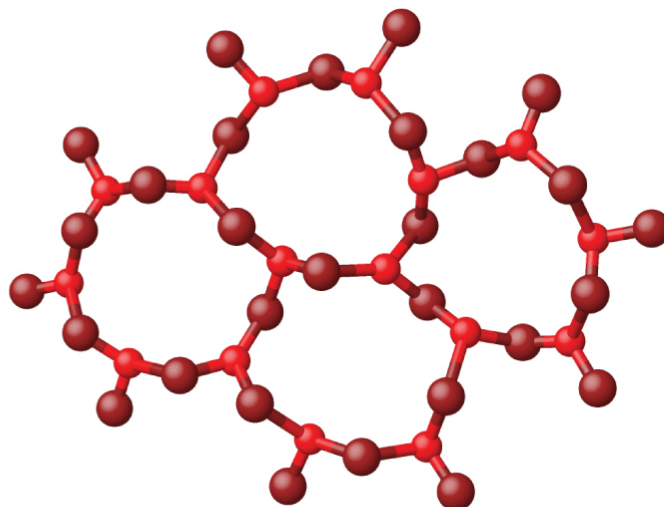
(a)   (b)

(a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong ([link]). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.
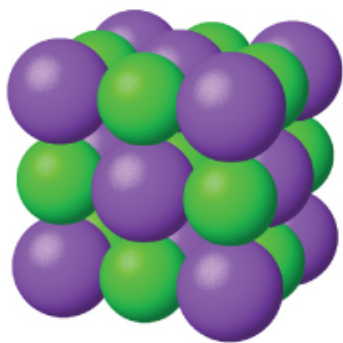
Sodium chloride is an ionic solid.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms [link]. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a "sea" of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.
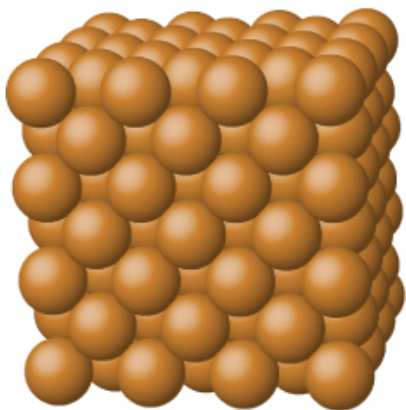
Copper is a metallic solid.

Covalent Network Solid

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in [link]. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.
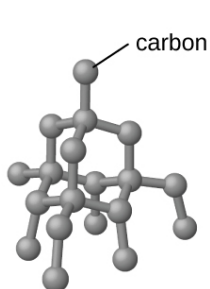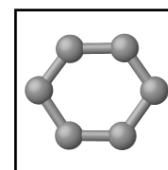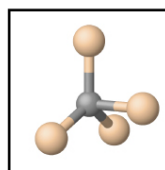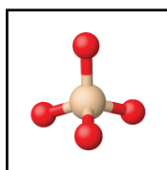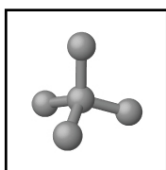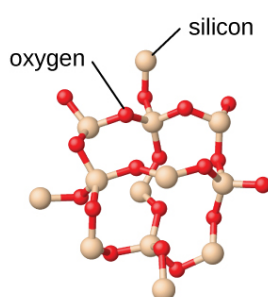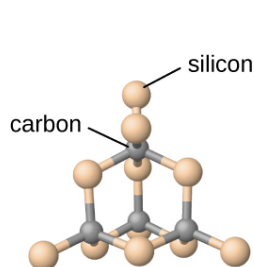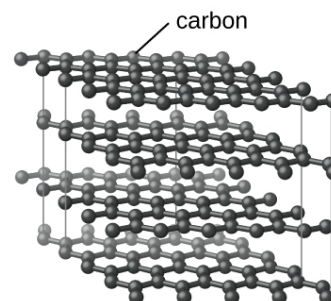
| diamond | silicon dioxide | silicon carbide | graphite |

A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

Molecular Solid

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in [link], are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below −200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).
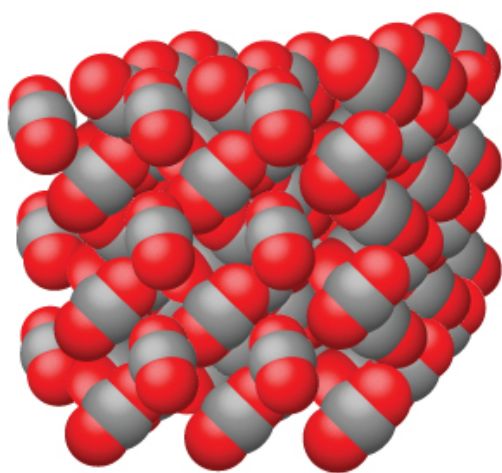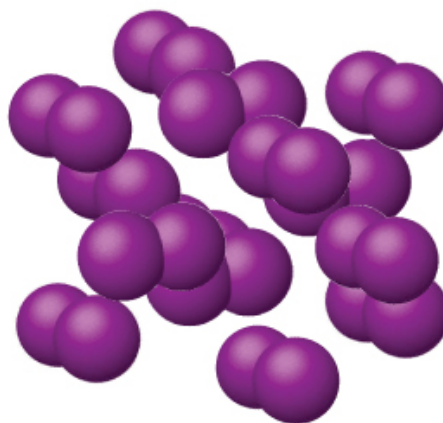
carbon dioxide   iodine

Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

Properties of Solids

A crystalline solid, like those listed in [link], has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous

solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Types of Crystalline Solids and Their Properties				
Type of Solid	**Type of Particles**	**Type of Attractions**	**Properties**	**Examples**
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	$NaCl$, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC

Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Note:

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in [link]. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

1.4 × 10^{-10} m
Distance between center of atoms

| diamond | graphite | Graphite surface |
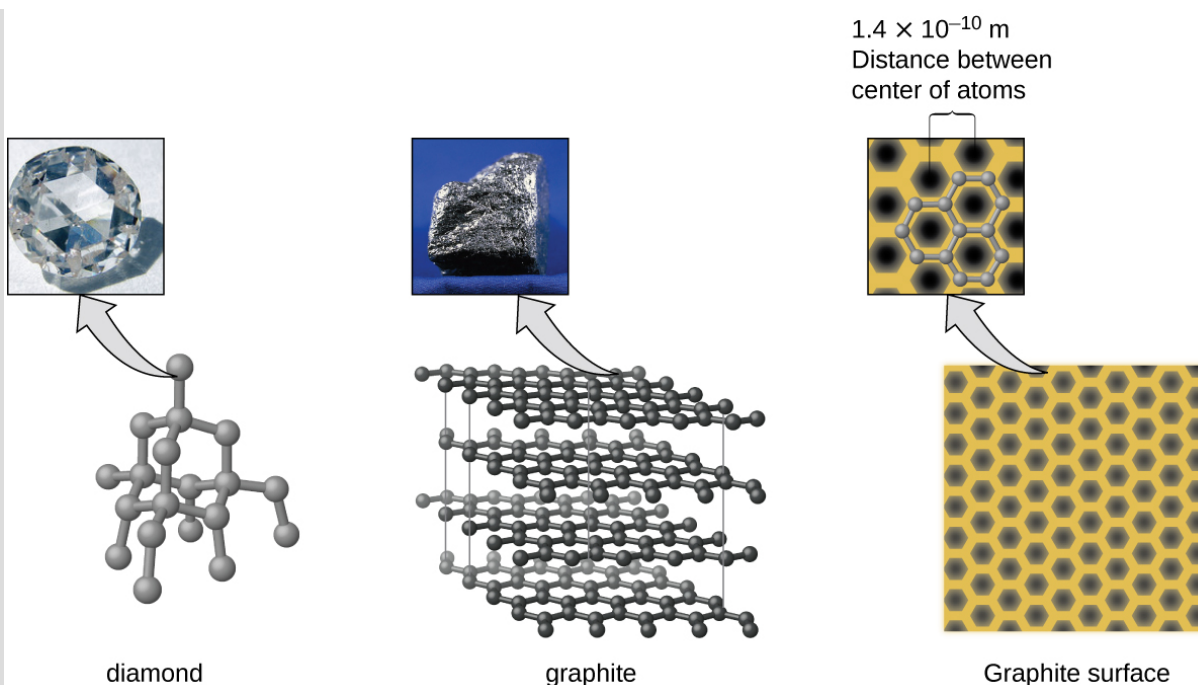
Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in [link], is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

Graphene sheet

Buckyball   **Nanotube**   **Stacked sheets**

Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.
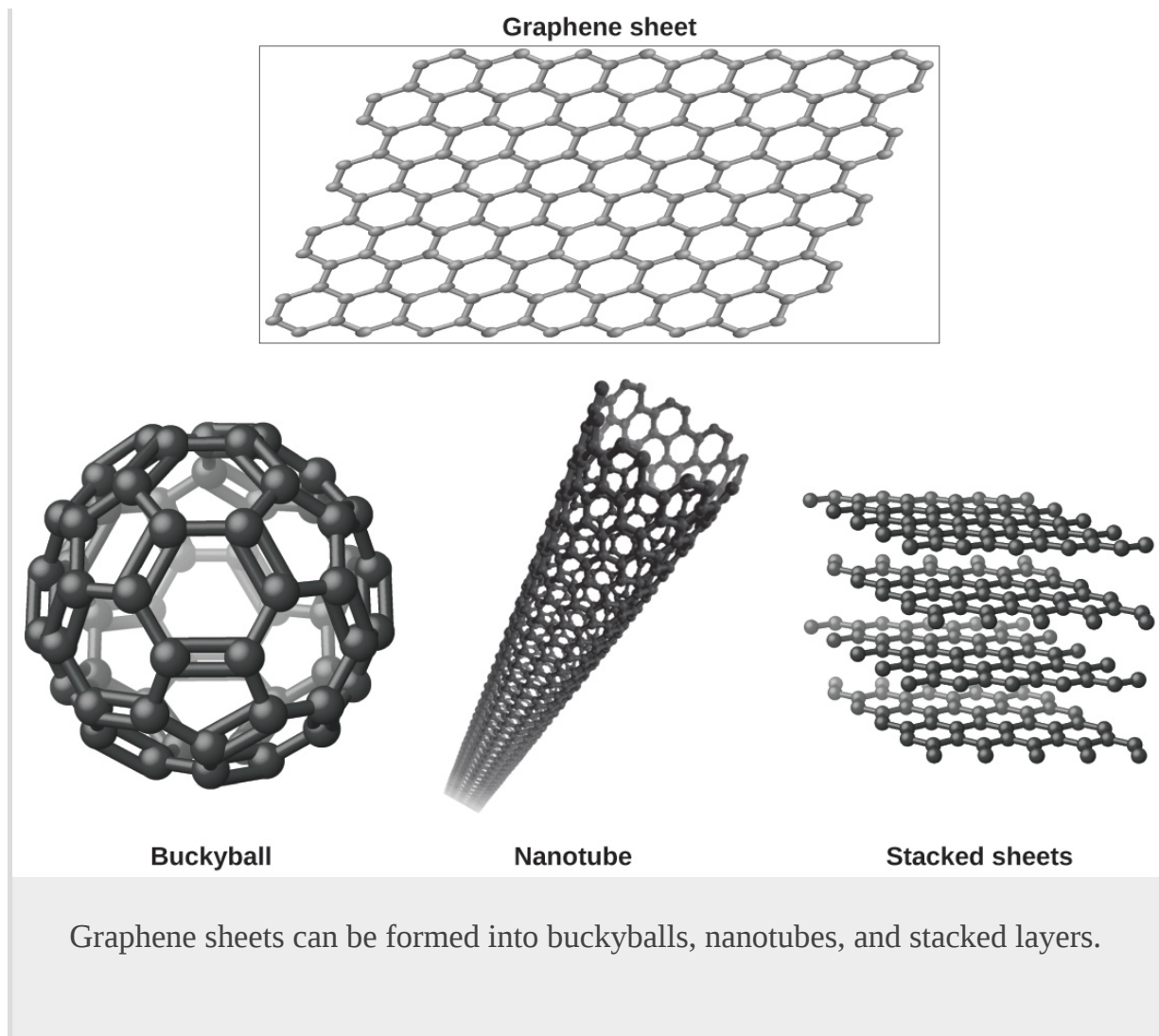
Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in [link]. **Vacancies** are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called **interstitial sites**, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals

are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.
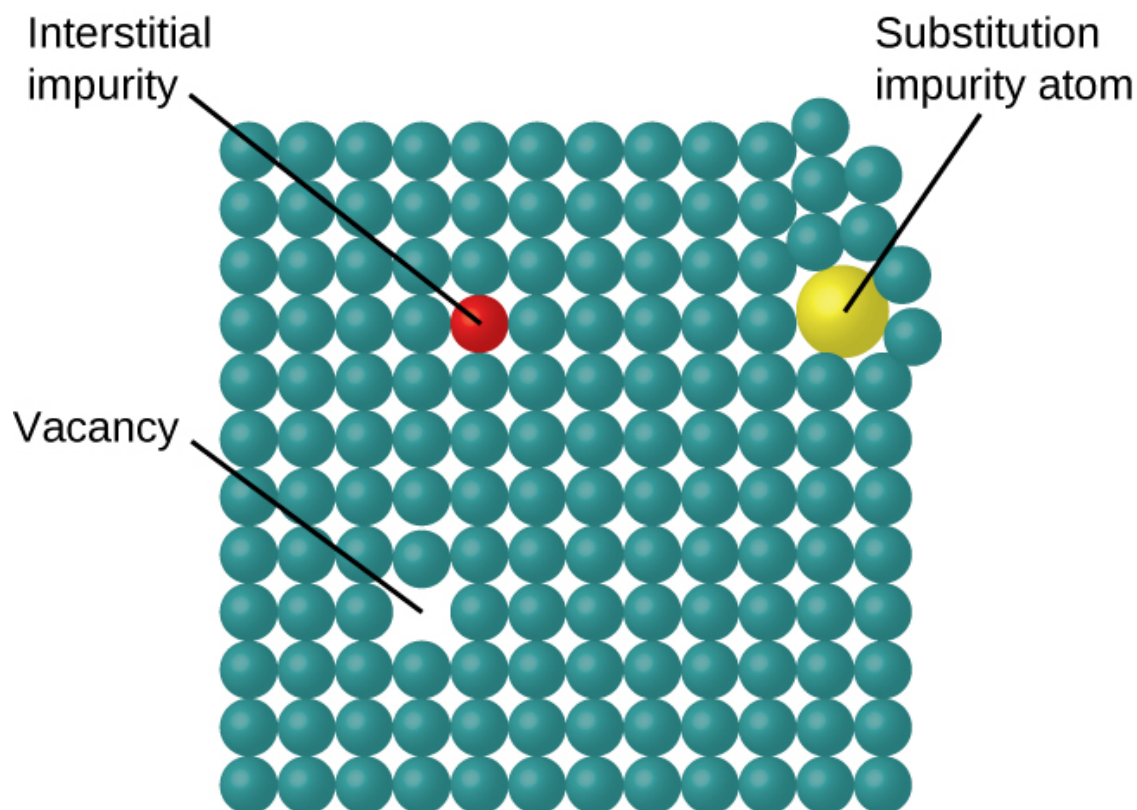
Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Key Concepts and Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some

crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Chemistry End of Chapter Exercises

Exercise:

   Problem: What types of liquids typically form amorphous solids?

Exercise:

   Problem:

   At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?

   (a) ionic

   (b) covalent network

   (c) metallic

   (d) amorphous

   (e) molecular crystals

   Solution:

   (e) molecular crystals

Exercise:

   Problem:

   As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

   (a) ionic

   (b) covalent network

   (c) metallic

   (d) amorphous

(e) molecular crystals

Exercise:

Problem:

Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

Solution:

Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

Exercise:

Problem:

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) SiO_2

(b) KCl

(c) Cu

(d) CO_2

(e) C (diamond)

(f) $BaSO_4$

(g) NH_3

(h) NH_4F

(i) C_2H_5OH

Exercise:

Problem:

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) $CaCl_2$

(b) SiC

(c) N_2

(d) Fe

(e) C (graphite)

(f) $CH_3CH_2CH_2CH_3$

(g) HCl

(h) NH_4NO_3

(i) K_3PO_4

Solution:

(a) ionic; (b) covalent network; (c) molecular; (d) metallic; (e) covalent network; (f) molecular; (g) molecular; (h) ionic; (i) ionic

Exercise:

Problem:

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

Exercise:

Problem:

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

Solution:

X = ionic; Y = metallic; Z = covalent network

Exercise:

Problem:

Identify the following substances as ionic, metallic, covalent network, or molecular solids:

Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

Exercise:

Problem:

Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

(a) ionic solid

(b) metallic solid

(c) molecular solid

(d) covalent network solid

Solution:

(b) metallic solid

Exercise:

Problem:

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

(a) ionic solid

(b) metallic solid

(c) molecular solid

(d) covalent network solid

Glossary

amorphous solid
  (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid
    solid whose particles are held together by covalent bonds

crystalline solid
    solid in which the particles are arranged in a definite repeating pattern

interstitial sites
    spaces between the regular particle positions in any array of atoms or ions

ionic solid
    solid composed of positive and negative ions held together by strong electrostatic
    attractions

metallic solid
    solid composed of metal atoms

molecular solid
    solid composed of neutral molecules held together by intermolecular forces of
    attraction

vacancy
    defect that occurs when a position that should contain an atom or ion is vacant

The Periodic Table

Periodic Table of the Elements

Period

Group

| 1 | | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 |

1
1 H 1.008 hydrogen — 2 He 4.003 helium

2
3 Li 6.94 lithium — 4 Be 9.012 beryllium — 5 B 10.81 boron — 6 C 12.01 carbon — 7 N 14.01 nitrogen — 8 O 16.00 oxygen — 9 F 19.00 fluorine — 10 Ne 20.18 neon

3
11 Na 22.99 sodium — 12 Mg 24.31 magnesium — 13 Al 26.98 aluminum — 14 Si 28.09 silicon — 15 P 30.97 phosphorus — 16 S 32.06 sulfur — 17 Cl 35.45 chlorine — 18 Ar 39.95 argon

Groups 3–12:
| 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |

4
19 K 39.10 potassium — 20 Ca 40.08 calcium — 21 Sc 44.96 scandium — 22 Ti 47.87 titanium — 23 V 50.94 vanadium — 24 Cr 52.00 chromium — 25 Mn 54.94 manganese — 26 Fe 55.85 iron — 27 Co 58.93 cobalt — 28 Ni 58.69 nickel — 29 Cu 63.55 copper — 30 Zn 65.38 zinc — 31 Ga 69.72 gallium — 32 Ge 72.63 germanium — 33 As 74.92 arsenic — 34 Se 78.97 selenium — 35 Br 79.90 bromine — 36 Kr 83.80 krypton

5
37 Rb 85.47 rubidium — 38 Sr 87.62 strontium — 39 Y 88.91 yttrium — 40 Zr 91.22 zirconium — 41 Nb 92.91 niobium — 42 Mo 95.95 molybdenum — 43 Tc [97] technetium — 44 Ru 101.1 ruthenium — 45 Rh 102.9 rhodium — 46 Pd 106.4 palladium — 47 Ag 107.9 silver — 48 Cd 112.4 cadmium — 49 In 114.8 indium — 50 Sn 118.7 tin — 51 Sb 121.8 antimony — 52 Te 127.6 tellurium — 53 I 126.9 iodine — 54 Xe 131.3 xenon

6
55 Cs 132.9 cesium — 56 Ba 137.3 barium — 57-71 La–Lu * — 72 Hf 178.5 hafnium — 73 Ta 180.9 tantalum — 74 W 183.8 tungsten — 75 Re 186.2 rhenium — 76 Os 190.2 osmium — 77 Ir 192.2 iridium — 78 Pt 195.1 platinum — 79 Au 197.0 gold — 80 Hg 200.6 mercury — 81 Tl 204.4 thallium — 82 Pb 207.2 lead — 83 Bi 209.0 bismuth — 84 Po [209] polonium — 85 At [210] astatine — 86 Rn [222] radon

7
87 Fr [223] francium — 88 Ra [226] radium — 89-103 Ac–Lr ** — 104 Rf [267] rutherfordium — 105 Db [270] dubnium — 106 Sg [271] seaborgium — 107 Bh [270] bohrium — 108 Hs [277] hassium — 109 Mt [276] meitnerium — 110 Ds [281] darmstadtium — 111 Rg [282] roentgenium — 112 Cn [285] copernicium — 113 Uut [285] ununtrium — 114 Fl [289] flerovium — 115 Uup [288] ununpentium — 116 Lv [293] livermorium — 117 Uus [294] ununseptium — 118 Uuo [294] ununoctium

* 57 La 138.9 lanthanum — 58 Ce 140.1 cerium — 59 Pr 140.9 praseodymium — 60 Nd 144.2 neodymium — 61 Pm [145] promethium — 62 Sm 150.4 samarium — 63 Eu 152.0 europium — 64 Gd 157.3 gadolinium — 65 Tb 158.9 terbium — 66 Dy 162.5 dysprosium — 67 Ho 164.9 holmium — 68 Er 167.3 erbium — 69 Tm 168.9 thulium — 70 Yb 173.1 ytterbium — 71 Lu 175.0 lutetium

** 89 Ac [227] actinium — 90 Th 232.0 thorium — 91 Pa 231.0 protactinium — 92 U 238.0 uranium — 93 Np [237] neptunium — 94 Pu [244] plutonium — 95 Am [243] americium — 96 Cm [247] curium — 97 Bk [247] berkelium — 98 Cf [251] californium — 99 Es [252] einsteinium — 100 Fm [257] fermium — 101 Md [258] mendelevium — 102 No [259] nobelium — 103 Lr [262] lawrencium

Atomic number → 1

H ← Symbol

1.008 ← Atomic mass

Name → hydrogen

Color Code

Metal	**Solid**
Metalloid	**Liquid**
Nonmetal	**Gas**

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

Equation:

$$
\begin{aligned}
1000 &= 1 \times 10^3 \\
100 &= 1 \times 10^2 \\
10 &= 1 \times 10^1 \\
1 &= 1 \times 10^0 \\
0.1 &= 1 \times 10^{-1} \\
0.001 &= 1 \times 10^{-3} \\
2386 &= 2.386 \times 1000 = 2.386 \times 10^3 \\
0.123 &= 1.23 \times 0.1 = 1.23 \times 10^{-1}
\end{aligned}
$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, $1{,}230{,}000{,}000 = 1.23 \times 10^9$, and $0.00000000036 = 3.6 \times 10^{-10}$.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Example:

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Multiplying Exponentials
Multiply 4.2×10^{-8} by 2.0×10^3.
Solution
Equation:

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Example:
Dividing Exponentials
Divide 3.6×10^5 by 6.0×10^{-4}.
Solution
Equation:

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Example:
Squaring Exponentials
Square the number 4.0×10^{-6}.
Solution

Equation:

$$\left(4.0 \times 10^{-6}\right)^2 = 4 \times 4 \times 10^{2 \times (-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Example:
Cubing Exponentials
Cube the number 2×10^4.
Solution
Equation:

$$\left(2 \times 10^4\right)^3 = 2 \times 2 \times 2 \times 10^{3 \times 4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Example:
Finding the Square Root of Exponentials
Find the square root of 1.6×10^{-7}.
Solution
Equation:

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

Example:
Addition and Subtraction with Significant Figures
Add 4.383 g and 0.0023 g.
Solution
Equation:

$$4.38\underline{3} \text{ g}$$
$$0.002\underline{3} \text{ g}$$
$$\overline{4.38\underline{5} \text{ g}}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 ("round up"). Do not change the retained digit if the digits that follow are less than 5 ("round down"). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm

Logarithms and Exponential Numbers		
Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.001	10^{-3}	−3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

Equation:

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

Equation:

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

Equation:

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.
   Equation:

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y$$

2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.
   Equation:

$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y$$

3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.
   Equation:

$$\log x^n = n\log x \text{ and } \ln x^n = n\ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.
Equation:

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

Equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Example:

Solving Quadratic Equations

Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution

Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

Equation:

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

Equation:

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

Equation:

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \ \text{and} \ x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (*x-y*) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (*x*), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (*y*).

When the value of *y* is changing as a function of *x* (that is, different values of *x* correspond to different values of *y*), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (*x,y*) data pairs.

Example:
Graphing the Dependence of *y* on *x*

x	*y*
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of *y* on *x*.
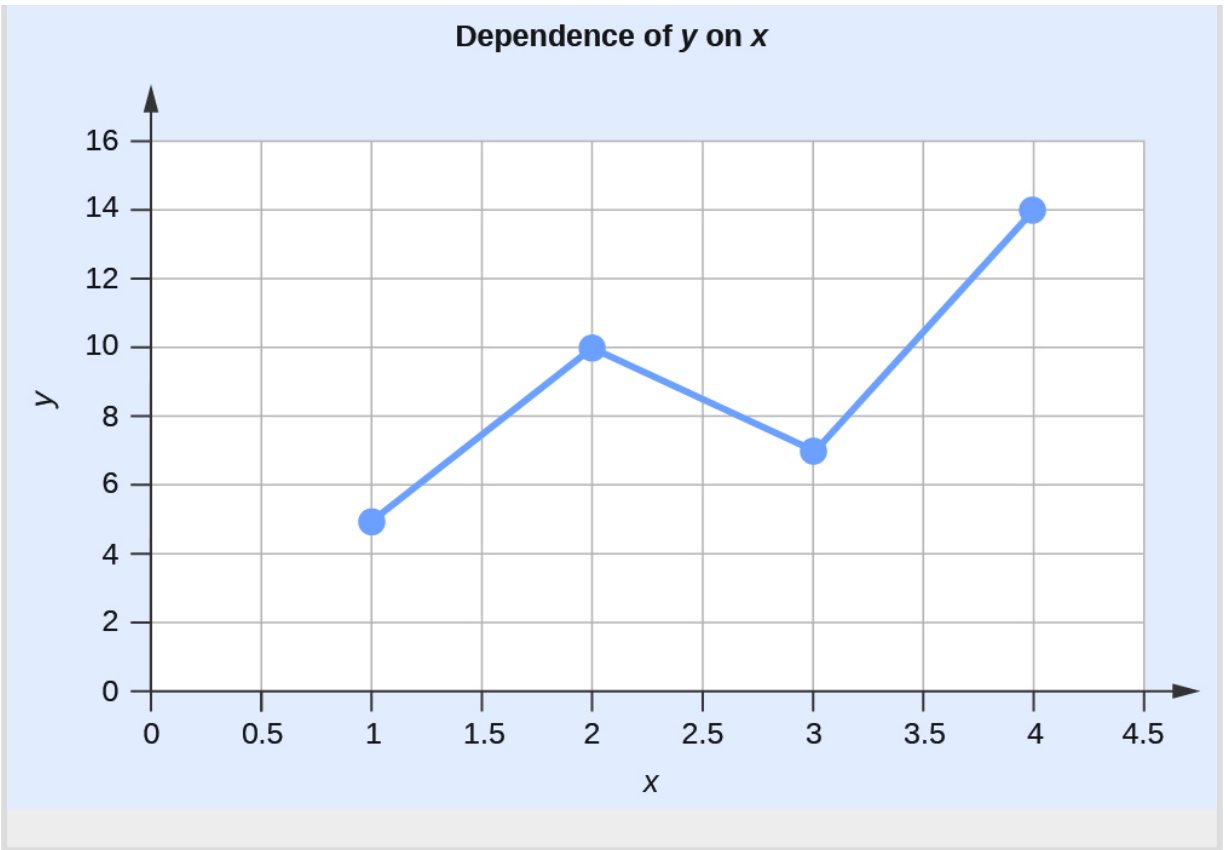
Dependence of *y* on *x*

If the function that describes the dependence of *y* on *x* is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Example:
Plotting Data Pairs
If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

x	$y = x^2 + 2$

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18

$y = x^2 + 2$
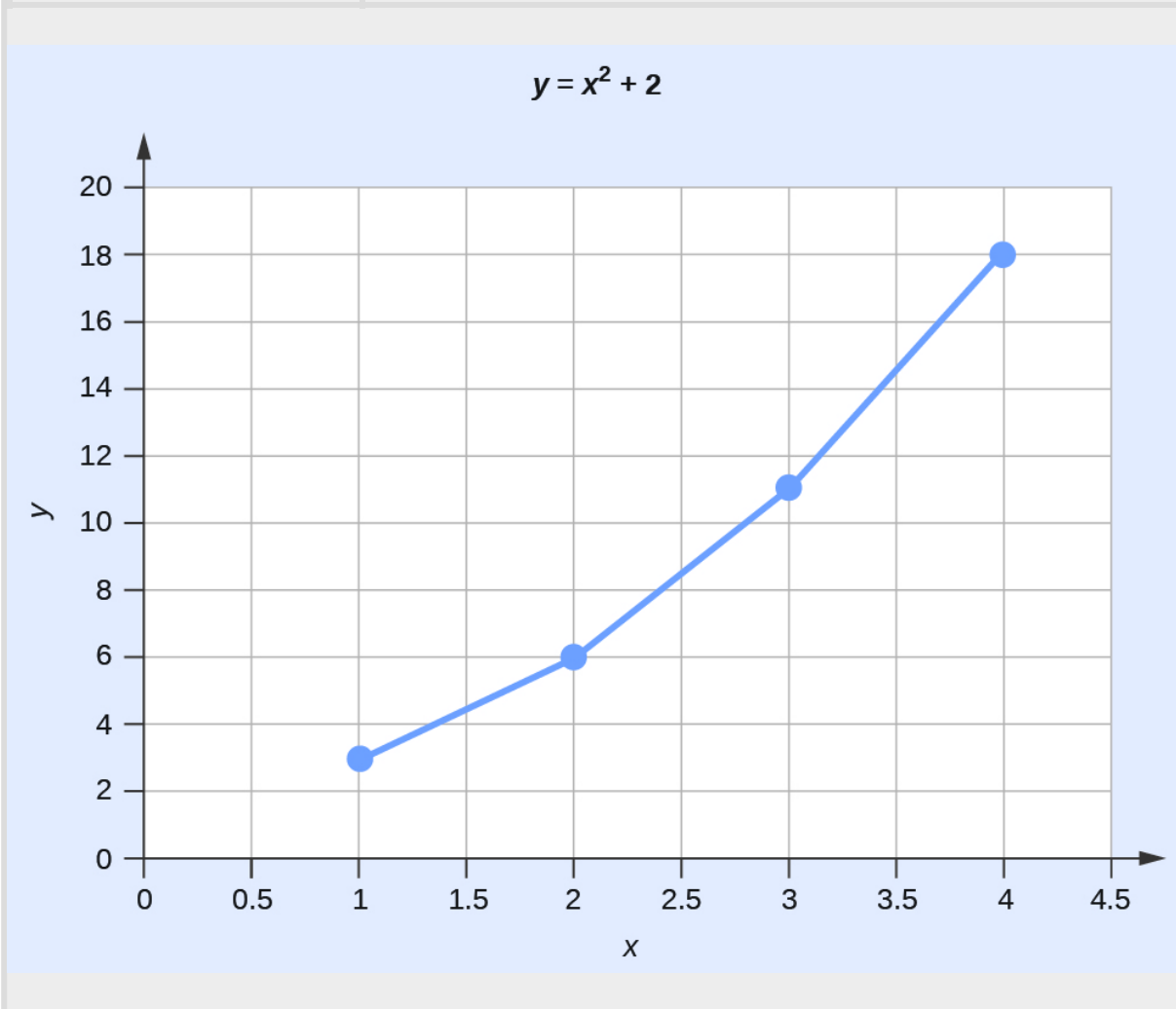
Units and Conversion Factors

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume

Units of Volume

liter (L)	$= 0.001 \text{ m}^3$ (exact, definition) $= 1000 \text{ cm}^3$ (exact, definition) $= 1.057$ (US) quarts	liquid quart (US)	$= 32$ (US) liquid ounces (exact, definition) $= 0.25$ (US) gallon (exact, definition) $= 0.9463 \text{ L}$
milliliter (mL)	$= 0.001 \text{ L}$ (exact, definition) $= 1 \text{ cm}^3$ (exact, definition)	dry quart	$= 1.1012 \text{ L}$
microliter (µL)	$= 10^{-6} \text{ L}$ (exact, definition) $= 10^{-3} \text{ cm}^3$ (exact, definition)	cubic foot (US)	$= 28.316 \text{ L}$

Units of Mass

gram (g)	$= 0.001 \text{ kg}$ (exact, definition)	ounce (oz) (avoirdupois)	$= 28.35 \text{ g}$

Units of Mass

milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy

4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)

Units of Energy	
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[footnote] BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10^5 Pa (exact, definition) = 10^5 kg m^{-1} s^{-2} (exact, definition)

Fundamental Physical Constants

Fundamental Physical Constants	
Name and Symbol	**Value**
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
Avogadro's number	6.0221367×10^{23} mol^{-1}
Boltzmann's constant (k)	1.380658×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
electron charge (e)	$1.60217733 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093897 \times 10^{-31}$ kg
Faraday's constant (F)	9.6485309×10^{4} C mol^{-1}
gas constant (R)	8.205784×10^{-2} L atm mol^{-1} K^{-1} = 8.314510 J mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 0 °C	22.41409 L mol^{-1}
molar volume of an ideal gas, 1 bar, 0 °C	22.71108 L mol^{-1}
neutron rest mass (m_n)	$1.6749274 \times 10^{-27}$ kg

Fundamental Physical Constants

Name and Symbol	Value
Planck's constant (h)	$6.6260755 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726231 \times 10^{-27}$ kg
Rydberg constant (R)	$1.0973731534 \times 10^{7}$ m^{-1} = $2.1798736 \times 10^{-18}$ J
speed of light (in vacuum) (c)	2.99792458×10^{8} m s^{-1}

Water Properties

Water Density (kg/m^3) at Different Temperatures (°C)	
Temperature[footnote] **Data for t < 0 °C are for supercooled water**	**Density**
0	999.8395
4	999.9720 (density maximum)
10	999.7026
15	999.1026
20	998.2071
22	997.7735
25	997.0479
30	995.6502
40	992.2
60	983.2
80	971.8
100	958.4
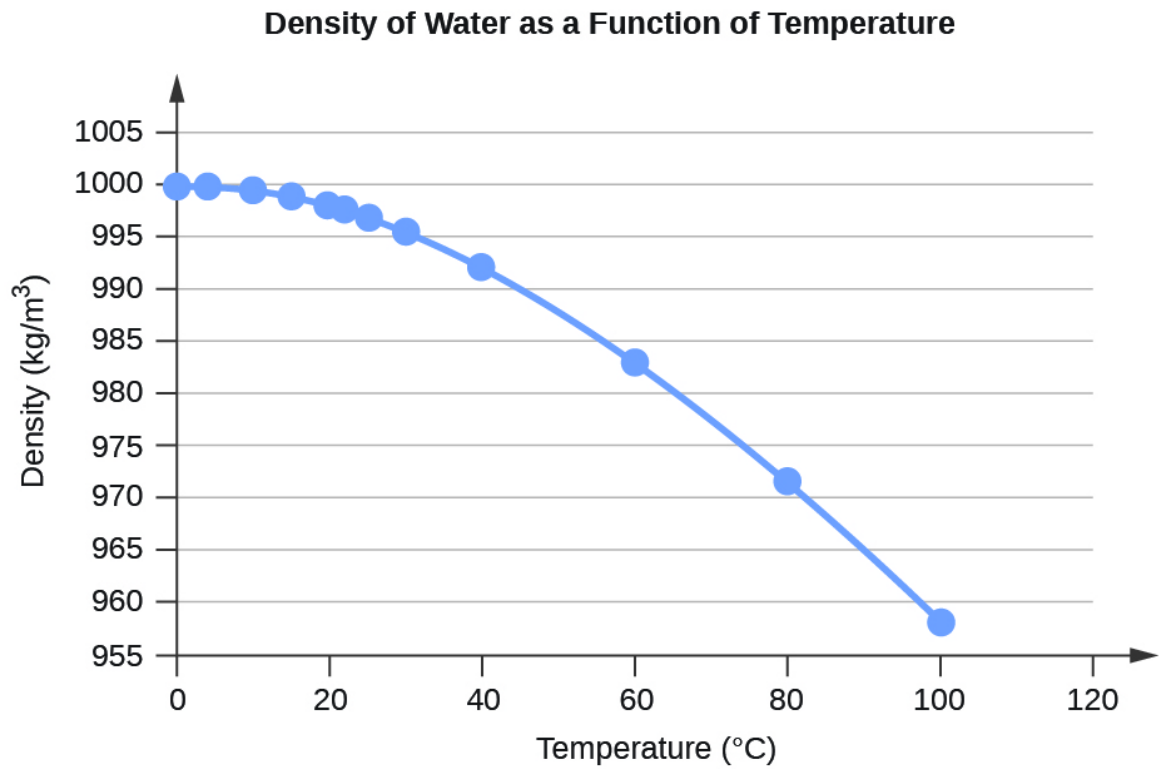
Density of Water as a Function of Temperature

Water Vapor Pressure at Different Temperatures (°C)		
Temperature	**Vapor Pressure (torr)**	**Vapor Pressure (Pa)**
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522

Water Vapor Pressure at Different Temperatures (°C)

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71

Water Vapor Pressure at Different Temperatures (°C)

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
95	633.9	84512.82
100	760.0	101324.7

Vapor Pressure as a Function of Temperature
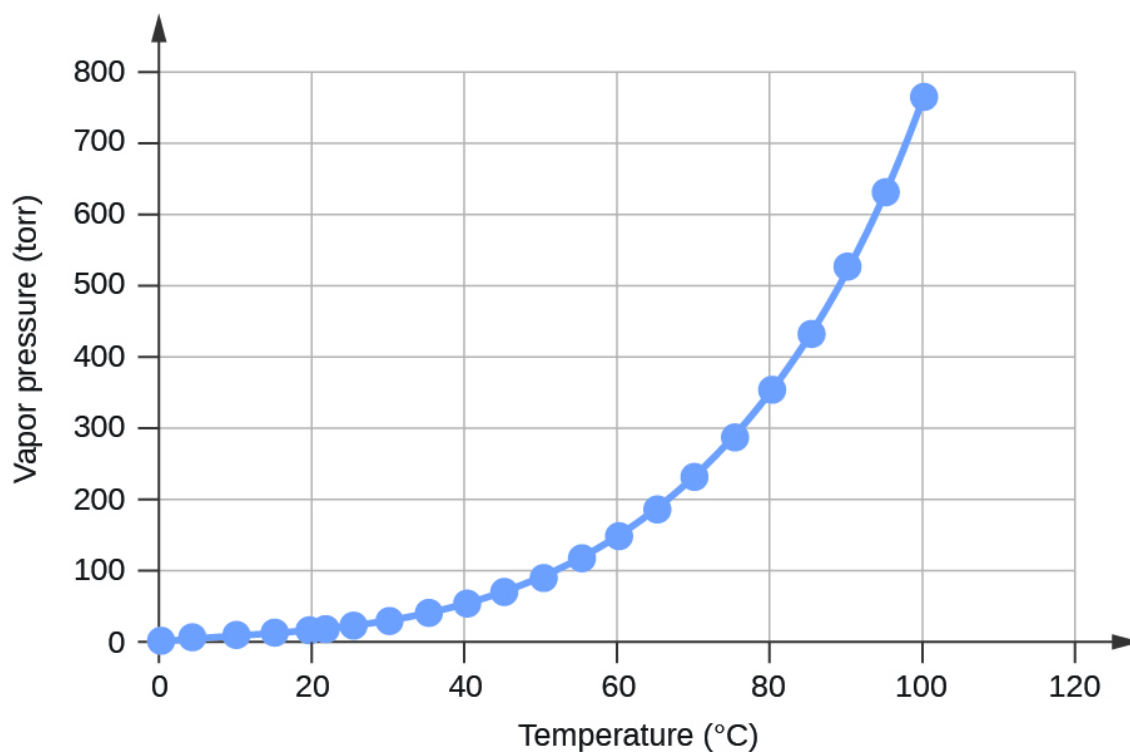
Water K_w and pK_w at Different Temperatures (°C)

Water K_w and pK_w at Different Temperatures (°C)		
Temperature	K_w 10^{-14}	pK_w [footnote] $pK_w = -\log_{10}(K_w)$
Temperature	K_w 10^{-14}	pK_w [footnote] $pK_w = -\log_{10}(K_w)$
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25

Water pK$_w$ as a Function of Temperature
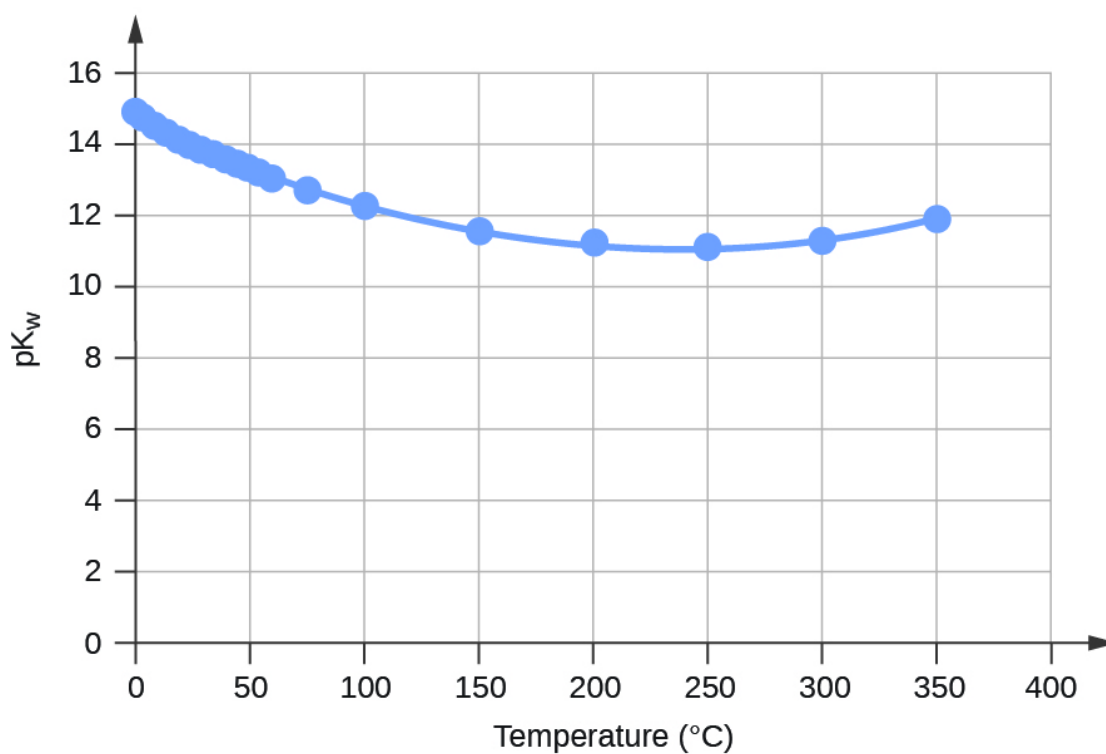
Specific Heat Capacity for Water
C°(H$_2$O(l)) = 4184 J·K^{-1}·kg^{-1} = 4.184 J·g^{-1}·°C^{-1}
C°(H$_2$O(s)) = 1864 J·K^{-1}·kg^{-1}
C°(H$_2$O(g)) = 2093 J·K^{-1}·kg^{-1}

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions		
	Temperature (K)	**ΔH (kJ/mol)**
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants
$K_f = 1.86°C·kg·mol^{-1}$ (cryoscopic constant)
$K_b = 0.51°C·kg·mol^{-1}$ (ebullioscopic constant)

Water Full-Range Spectral Absorption Curve
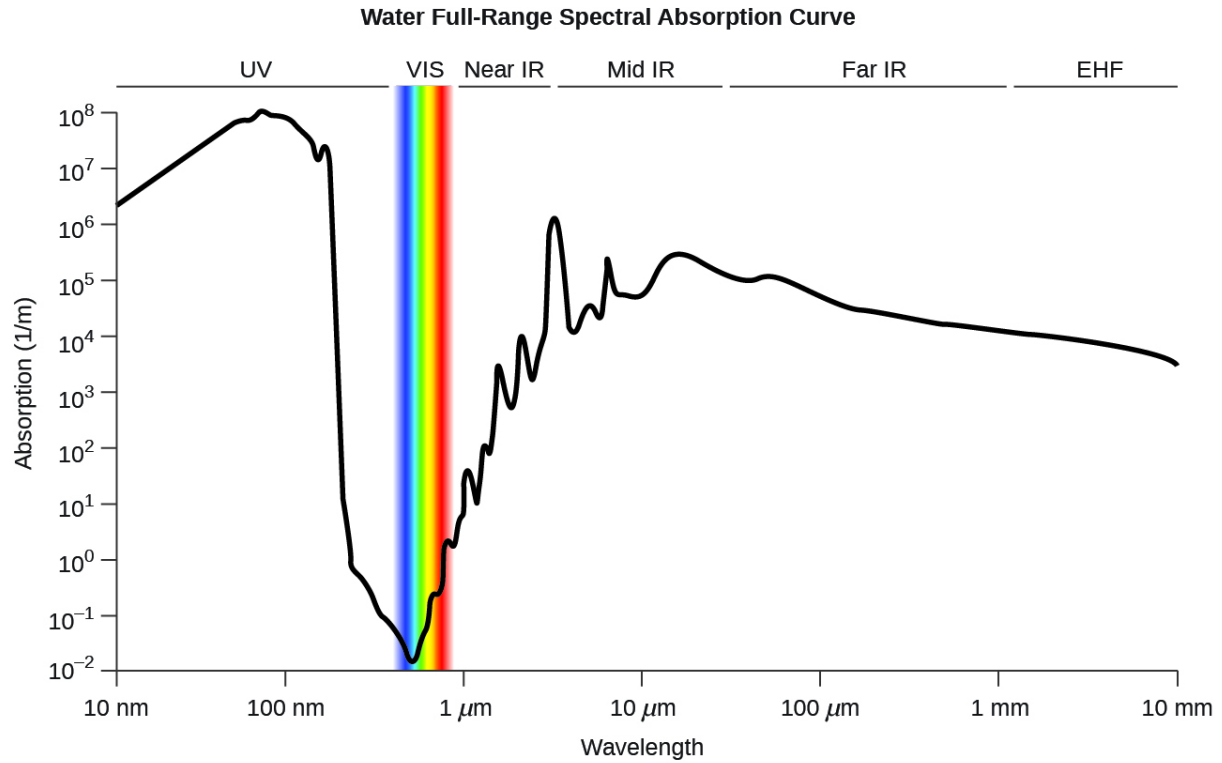
Water full-range spectral absorption curve. This curve shows the full-range spectral absorption for water. The *y*-axis signifies the absorption in 1/cm. If we divide 1 by this value, we will obtain the length of the path (in cm) after which the intensity of a light beam passing through water decays by a factor of the base of the natural logarithm e (e = 2.718281828).

Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases			
Acid or Base[footnote] Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.	**Density (g/mL) [footnote]** This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.	**Percentage by Mass**	**Molarity**
acetic acid, glacial	1.05	99.5%	17.4

aqueous ammonia[footnote] This solution is sometimes called "ammonium hydroxide," although this term is not chemically accurate.	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol⁻¹)	S_{298}° (J K⁻¹ mol⁻¹)
aluminum			
Al(s)	0	0	28.3
Al(g)	324.4	285.7	164.54
Al³⁺(aq)	−531	−485	−321.7
Al₂O₃(s)	−1676	−1582	50.92
AlF₃(s)	−1510.4	−1425	66.5
AlCl₃(s)	−704.2	−628.8	110.67
AlCl₃·6H₂O(s)	−2691.57	−2269.40	376.56
Al₂S₃(s)	−724.0	−492.4	116.9
Al₂(SO₄)₃(s)	−3445.06	−3506.61	239.32
antimony			

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
Sb(s)	0	0	45.69
Sb(g)	262.34	222.17	180.16
Sb$_4$O$_6$(s)	−1440.55	−1268.17	220.92
SbCl$_3$(g)	−313.8	−301.2	337.80
SbCl$_5$(g)	−394.34	−334.29	401.94
Sb$_2$S$_3$(s)	−174.89	−173.64	182.00
SbCl$_3$(s)	−382.17	−323.72	184.10
SbOCl(s)	−374.0	—	—
arsenic			
As(s)	0	0	35.1
As(g)	302.5	261.0	174.21
As$_4$(g)	143.9	92.4	314
As$_4$O$_6$(s)	−1313.94	−1152.52	214.22
As$_2$O$_5$(s)	−924.87	−782.41	105.44

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
AsCl$_3$(g)	−261.50	−248.95	327.06
As$_2$S$_3$(s)	−169.03	−168.62	163.59
AsH$_3$(g)	66.44	68.93	222.78
H$_3$AsO$_4$(s)	−906.3	—	—
barium			
Ba(s)	0	0	62.5
Ba(g)	180	146	170.24
Ba^{2+}(aq)	−537.6	−560.8	9.6
BaO(s)	−548.0	−520.3	72.1
BaCl$_2$(s)	−855.0	−806.7	123.7
BaSO$_4$(s)	−1473.2	−1362.3	132.2
beryllium			
Be(s)	0	0	9.50
Be(g)	324.3	286.6	136.27
BeO(s)	−609.4	−580.1	13.8

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
bismuth			
Bi(s)	0	0	56.74
Bi(g)	207.1	168.2	187.00
Bi$_2$O$_3$(s)	−573.88	−493.7	151.5
BiCl$_3$(s)	−379.07	−315.06	176.98
Bi$_2$S$_3$(s)	−143.1	−140.6	200.4
boron			
B(s)	0	0	5.86
B(g)	565.0	521.0	153.4
B$_2$O$_3$(s)	−1273.5	−1194.3	53.97
B$_2$H$_6$(g)	36.4	87.6	232.1
H$_3$BO$_3$(s)	−1094.33	−968.92	88.83
BF$_3$(g)	−1136.0	−1119.4	254.4
BCl$_3$(g)	−403.8	−388.7	290.1
B$_3$N$_3$H$_6$(l)	−540.99	−392.79	199.58

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$HBO_2(s)$	−794.25	−723.41	37.66
bromine			
$Br_2(l)$	0	0	152.23
$Br_2(g)$	30.91	3.142	245.5
$Br(g)$	111.88	82.429	175.0
$Br^-(aq)$	−120.9	−102.82	80.71
$BrF_3(g)$	−255.60	−229.45	292.42
$HBr(g)$	−36.3	−53.43	198.7
cadmium			
$Cd(s)$	0	0	51.76
$Cd(g)$	112.01	77.41	167.75
$Cd^{2+}(aq)$	−75.90	−77.61	−73.2
$CdO(s)$	−258.2	−228.4	54.8
$CdCl_2(s)$	−391.5	−343.9	115.3
$CdSO_4(s)$	−933.3	−822.7	123.0

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol⁻¹)	S_{298}° (J K⁻¹ mol⁻¹)
CdS(s)	−161.9	−156.5	64.9
calcium			
Ca(s)	0	0	41.6
Ca(g)	178.2	144.3	154.88
Ca²⁺(aq)	−542.96	−553.04	−55.2
CaO(s)	−634.9	−603.3	38.1
Ca(OH)₂(s)	−985.2	−897.5	83.4
CaSO₄(s)	−1434.5	−1322.0	106.5
CaSO₄·2H₂O(s)	−2022.63	−1797.45	194.14
CaCO₃(s) (calcite)	−1220.0	−1081.4	110.0
CaSO₃·H₂O(s)	−1752.68	−1555.19	184.10
carbon			
C(s) (graphite)	0	0	5.740
C(s) (diamond)	1.89	2.90	2.38

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
C(g)	716.681	671.2	158.1
CO(g)	−110.52	−137.15	197.7
CO$_2$(g)	−393.51	−394.36	213.8
CO$_3{}^{2-}$(aq)	−677.1	−527.8	−56.9
CH$_4$(g)	−74.6	−50.5	186.3
CH$_3$OH(l)	−239.2	−166.6	126.8
CH$_3$OH(g)	−201.0	−162.3	239.9
CCl$_4$(l)	−128.2	−62.5	214.4
CCl$_4$(g)	−95.7	−58.2	309.7
CHCl$_3$(l)	−134.1	−73.7	201.7
CHCl$_3$(g)	−103.14	−70.34	295.71
CS$_2$(l)	89.70	65.27	151.34
CS$_2$(g)	116.9	66.8	238.0
C$_2$H$_2$(g)	227.4	209.2	200.9
C$_2$H$_4$(g)	52.4	68.4	219.3

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3^-(aq)$	–691.11	–587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol⁻¹)	S_{298}° (J K⁻¹ mol⁻¹)
HCN(*l*)	108.9	125.0	112.8
HCN(*g*)	135.5	124.7	201.8
cesium			
Cs⁺(*aq*)	–248	–282.0	133
chlorine			
Cl₂(*g*)	0	0	223.1
Cl(*g*)	121.3	105.70	165.2
Cl⁻(*aq*)	–167.2	–131.2	56.5
ClF(*g*)	–54.48	–55.94	217.78
ClF₃(*g*)	–158.99	–118.83	281.50
Cl₂O(*g*)	80.3	97.9	266.2
Cl₂O₇(*l*)	238.1	—	—
Cl₂O₇(*g*)	272.0	—	—
HCl(*g*)	–92.307	–95.299	186.9
HClO₄(*l*)	–40.58	—	—

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
chromium			
Cr(s)	0	0	23.77
Cr(g)	396.6	351.8	174.50
$CrO_4{}^{2-}$(aq)	–881.2	–727.8	50.21
$Cr_2O_7{}^{2-}$(aq)	–1490.3	–1301.1	261.9
Cr_2O_3(s)	–1139.7	–1058.1	81.2
CrO_3(s)	–589.5	—	—
$(NH_4)_2Cr_2O_7$(s)	–1806.7	—	—
cobalt			
Co(s)	0	0	30.0
Co^{2+}(aq)	–67.4	–51.5	–155
Co^{3+}(aq)	92	134	–305.0
CoO(s)	–237.9	–214.2	52.97
Co_3O_4(s)	–910.02	–794.98	114.22
$Co(NO_3)_2$(s)	–420.5	—	—

Standard Thermodynamic Properties for Selected Substances

Substance	$\Delta H_{\mathrm{f}}^{\circ}$ (kJ mol$^-$)	$\Delta G_{\mathrm{f}}^{\circ}$ (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
copper			
Cu(s)	0	0	33.15
Cu(g)	338.32	298.58	166.38
Cu$^+$(aq)	51.9	50.2	–26
Cu^{2+}(aq)	64.77	65.49	–99.6
CuO(s)	–157.3	–129.7	42.63
Cu$_2$O(s)	–168.6	–146.0	93.14
CuS(s)	–53.1	–53.6	66.5
Cu$_2$S(s)	–79.5	–86.2	120.9
CuSO$_4$(s)	–771.36	–662.2	109.2
Cu(NO$_3$)$_2$(s)	–302.9	—	—
fluorine			
F$_2$(g)	0	0	202.8
F(g)	79.4	62.3	158.8
F$^-$(aq)	–332.6	–278.8	–13.8

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
F$_2$O(g)	24.7	41.9	247.43
HF(g)	−273.3	−275.4	173.8
hydrogen			
H$_2$(g)	0	0	130.7
H(g)	217.97	203.26	114.7
H$^+$(aq)	0	0	0
OH$^-$(aq)	−230.0	−157.2	−10.75
H$_3$O$^+$(aq)	−285.8		69.91
H$_2$O(l)	−285.83	−237.1	70.0
H$_2$O(g)	−241.82	−228.59	188.8
H$_2$O$_2$(l)	−187.78	−120.35	109.6
H$_2$O$_2$(g)	−136.3	−105.6	232.7
HF(g)	−273.3	−275.4	173.8
HCl(g)	−92.307	−95.299	186.9
HBr(g)	−36.3	−53.43	198.7

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol⁻¹)	S_{298}° (J K⁻¹ mol⁻¹)
HI(g)	26.48	1.70	206.59
H₂S(g)	−20.6	−33.4	205.8
H₂Se(g)	29.7	15.9	219.0
iodine			
I₂(s)	0	0	116.14
I₂(g)	62.438	19.3	260.7
I(g)	106.84	70.2	180.8
I⁻(aq)	−55.19	−51.57	11.13
IF(g)	95.65	−118.49	236.06
ICl(g)	17.78	−5.44	247.44
IBr(g)	40.84	3.72	258.66
IF₇(g)	−943.91	−818.39	346.44
HI(g)	26.48	1.70	206.59
iron			
Fe(s)	0	0	27.3

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
Fe(g)	416.3	370.7	180.5
Fe^{2+}(aq)	−89.1	−78.90	−137.7
Fe^{3+}(aq)	−48.5	−4.7	−315.9
Fe$_2$O$_3$(s)	−824.2	−742.2	87.40
Fe$_3$O$_4$(s)	−1118.4	−1015.4	146.4
Fe(CO)$_5$(l)	−774.04	−705.42	338.07
Fe(CO)$_5$(g)	−733.87	−697.26	445.18
FeCl$_2$(s)	−341.79	−302.30	117.95
FeCl$_3$(s)	−399.49	−334.00	142.3
FeO(s)	−272.0	−255.2	60.75
Fe(OH)$_2$(s)	−569.0	−486.5	88.
Fe(OH)$_3$(s)	−823.0	−696.5	106.7
FeS(s)	−100.0	−100.4	60.29
Fe$_3$C(s)	25.10	20.08	104.60
lead			

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
Pb(s)	0	0	64.81
Pb(g)	195.2	162.	175.4
Pb^{2+}(aq)	−1.7	−24.43	10.5
PbO(s) (yellow)	−217.32	−187.89	68.70
PbO(s) (red)	−218.99	−188.93	66.5
Pb(OH)$_2$(s)	−515.9	—	—
PbS(s)	−100.4	−98.7	91.2
Pb(NO$_3$)$_2$(s)	−451.9	—	—
PbO$_2$(s)	−277.4	−217.3	68.6
PbCl$_2$(s)	−359.4	−314.1	136.0
lithium			
Li(s)	0	0	29.1
Li(g)	159.3	126.6	138.8
Li$^+$(aq)	−278.5	−293.3	13.4
LiH(s)	−90.5	−68.3	20.0

Standard Thermodynamic Properties for Selected Substances

Substance	$\Delta H_{\mathrm{f}}^{\circ}$ (kJ mol$^-$)	$\Delta G_{\mathrm{f}}^{\circ}$ (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
Li(OH)(s)	–487.5	–441.5	42.8
LiF(s)	–616.0	–587.5	35.7
$Li_2CO_3(s)$	–1216.04	–1132.19	90.17
magnesium			
$Mg^{2+}(aq)$	–466.9	–454.8	–138.1
manganese			
Mn(s)	0	0	32.0
Mn(g)	280.7	238.5	173.7
$Mn^{2+}(aq)$	–220.8	–228.1	–73.6
MnO(s)	–385.2	–362.9	59.71
$MnO_2(s)$	–520.03	–465.1	53.05
$Mn_2O_3(s)$	–958.97	–881.15	110.46
$Mn_3O_4(s)$	–1378.83	–1283.23	155.64
$MnO_4^-(aq)$	–541.4	–447.2	191.2

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
MnO$_4$ $^{2-}$(aq)	−653.0	−500.7	59
mercury			
Hg(l)	0	0	75.9
Hg(g)	61.4	31.8	175.0
Hg^{2+}(aq)		164.8	
Hg^{2+}(aq)	172.4	153.9	84.5
HgO(s) (red)	−90.83	−58.5	70.29
HgO(s) (yellow)	−90.46	−58.43	71.13
HgCl$_2$(s)	−224.3	−178.6	146.0
Hg$_2$Cl$_2$(s)	−265.4	−210.7	191.6
HgS(s) (red)	−58.16	−50.6	82.4
HgS(s) (black)	−53.56	−47.70	88.28
HgSO$_4$(s)	−707.51	−594.13	0.00
nickel			
Ni^{2+}(aq)	−64.0	−46.4	−159

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
nitrogen			
$N_2(g)$	0	0	191.6
$N(g)$	472.704	455.5	153.3
$NO(g)$	90.25	87.6	210.8
$NO_2(g)$	33.2	51.30	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_3(g)$	83.72	139.41	312.17
$NO_3^-(aq)$	−205.0	−108.7	146.4
$N_2O_4(g)$	11.1	99.8	304.4
$N_2O_5(g)$	11.3	115.1	355.7
$NH_3(g)$	−45.9	−16.5	192.8
$NH_4^+(aq)$	−132.5	−79.31	113.4
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	−365.56	−183.87	151.08

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol⁻¹)	S_{298}° (J K⁻¹ mol⁻¹)
$NH_4Cl(s)$	−314.43	−202.87	94.6
$NH_4Br(s)$	−270.8	−175.2	113.0
$NH_4I(s)$	−201.4	−112.5	117.0
$NH_4NO_2(s)$	−256.5	—	—
$HNO_3(l)$	−174.1	−80.7	155.6
$HNO_3(g)$	−133.9	−73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
$O(g)$	249.17	231.7	161.1
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$PCl_3(g)$	−287.0	−267.8	311.78
$PCl_5(g)$	−374.9	−305.0	364.4
$P_4O_6(s)$	−1640.1	—	—
$P_4O_{10}(s)$	−2984.0	−2697.0	228.86
$PO_4{}^{3-}(aq)$	−1277	−1019	−222
$HPO_3(s)$	−948.5	—	—
$HPO_4{}^{2-}(aq)$	−1292.1	−1089.3	−33
$H_2PO_4{}^{2-}(aq)$	−1296.3	−1130.4	90.4
$H_3PO_2(s)$	−604.6	—	—
$H_3PO_3(s)$	−964.4	—	—
$H_3PO_4(s)$	−1279.0	−1119.1	110.50
$H_3PO_4(l)$	−1266.9	−1124.3	110.5
$H_4P_2O_7(s)$	−2241.0	—	—
$POCl_3(l)$	−597.1	−520.8	222.5
$POCl_3(g)$	−558.5	−512.9	325.5

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
potassium			
K(s)	0	0	64.7
K(g)	89.0	60.5	160.3
K$^+$(aq)	−252.4	−283.3	102.5
KF(s)	−576.27	−537.75	66.57
KCl(s)	−436.5	−408.5	82.6
rubidium			
Rb$^+$(aq)	−246	−282.2	124
silicon			
Si(s)	0	0	18.8
Si(g)	450.0	405.5	168.0
SiO$_2$(s)	−910.7	−856.3	41.5
SiH$_4$(g)	34.3	56.9	204.6
H$_2$SiO$_3$(s)	−1188.67	−1092.44	133.89

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$H_4SiO_4(s)$	$-$1481.14	−1333.02	192.46
$SiF_4(g)$	−1615.0	−1572.8	282.8
$SiCl_4(l)$	−687.0	−619.8	239.7
$SiCl_4(g)$	−662.75	−622.58	330.62
$SiC(s, beta\ cubic)$	−73.22	−70.71	16.61
$SiC(s, alpha\ hexagonal)$	−71.55	−69.04	16.48
silver			
$Ag(s)$	0	0	42.55
$Ag(g)$	284.9	246.0	172.89
$Ag^+(aq)$	105.6	77.11	72.68
$Ag_2O(s)$	−31.05	−11.20	121.3
$AgCl(s)$	−127.0	−109.8	96.3
$Ag_2S(s)$	−32.6	−40.7	144.0
sodium			

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol⁻¹)	S_{298}° (J K⁻¹ mol⁻¹)
Na(s)	0	0	51.3
Na(g)	107.5	77.0	153.7
Na⁺(aq)	−240.1	−261.9	59
Na₂O(s)	−414.2	−375.5	75.1
NaCl(s)	−411.2	−384.1	72.1
strontium			
Sr²⁺(aq)	−545.8	−557.3	−32.6
sulfur			
S₈(s) (rhombic)	0	0	256.8
S(g)	278.81	238.25	167.82
S²⁻(aq)	41.8	83.7	22
SO₂(g)	−296.83	−300.1	248.2
SO₃(g)	−395.72	−371.06	256.76
SO₄²⁻(aq)	−909.3	−744.5	20.1
S₂O₃²⁻(aq)	−648.5	−522.5	67

Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol⁻¹)	S_{298}° (J K⁻¹ mol⁻¹)
$H_2S(g)$	–20.6	–33.4	205.8
$HS^-(aq)$	–17.7	12.6	61.1
$H_2SO_4(l)$	–813.989	690.00	156.90
$HSO_4{}^{2-}(aq)$	–885.75	–752.87	126.9
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
$SO_2Cl_2(g)$	–354.80	–310.45	311.83
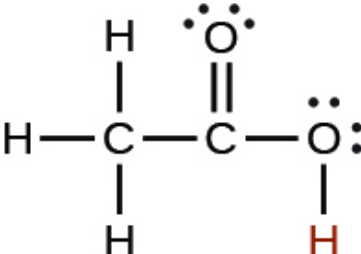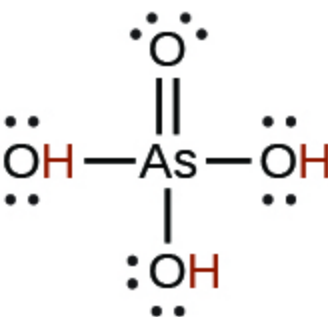
Standard Thermodynamic Properties for Selected Substances

Substance	$\Delta H_\mathrm{f}^{\circ}$ (kJ mol$^-$)	$\Delta G_\mathrm{f}^{\circ}$ (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
tin			
Sn(s)	0	0	51.2
Sn(g)	301.2	266.2	168.5
SnO(s)	−285.8	−256.9	56.5
SnO$_2$(s)	−577.6	−515.8	49.0
SnCl$_4$(l)	−511.3	−440.1	258.6
SnCl$_4$(g)	−471.5	−432.2	365.8
titanium			
Ti(s)	0	0	30.7
Ti(g)	473.0	428.4	180.3
TiO$_2$(s)	−944.0	−888.8	50.6
TiCl$_4$(l)	−804.2	−737.2	252.4
TiCl$_4$(g)	−763.2	−726.3	353.2
tungsten			
W(s)	0	0	32.6
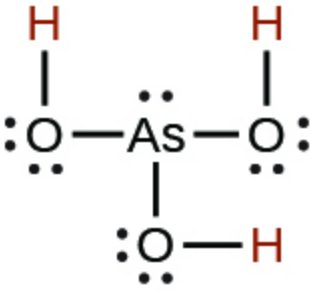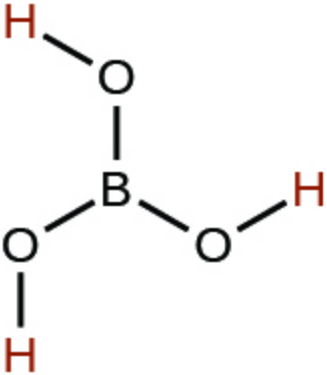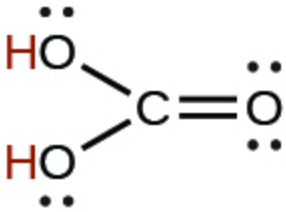
Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
W(g)	849.4	807.1	174.0
WO$_3$(s)	–842.9	–764.0	75.9
zinc			
Zn(s)	0	0	41.6
Zn(g)	130.73	95.14	160.98
Zn^{2+}(aq)	–153.9	–147.1	–112.1
ZnO(s)	–350.5	–320.5	43.7
ZnCl$_2$(s)	–415.1	–369.43	111.5
ZnS(s)	–206.0	–201.3	57.7
ZnSO$_4$(s)	–982.8	–871.5	110.5
ZnCO$_3$(s)	–812.78	–731.57	82.42
complexes			
[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$, *cis*	–898.7	—	—
[Co(NH$_3$)$_4$(NO$_2$)$_2$]NO$_3$, *trans*	–896.2	—	—
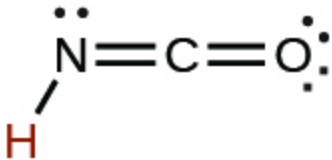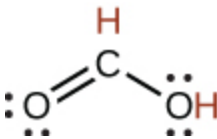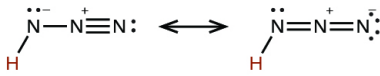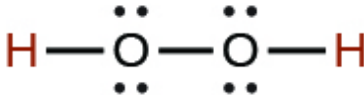
Standard Thermodynamic Properties for Selected Substances

Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
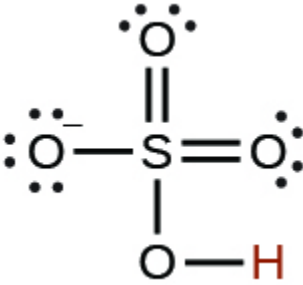
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol$^-$)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$[Co(NH_3)_5Cl]Cl_2$	−1017.1	−582.5	366.1
$[Pt(NH_3)_4]Cl_2$	−725.5	—	—
$[Ni(NH_3)_6]Cl_2$	−994.1	—	—
$[Ni(NH_3)_6]Br_2$	−923.8	—	—
$[Ni(NH_3)_6]I_2$	−808.3	—	—
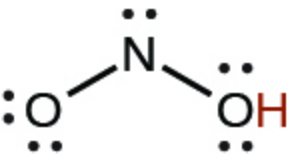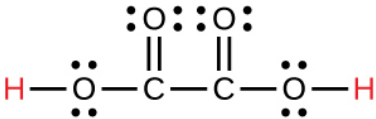
Ionization Constants of Weak Acids

Ionization Constants of Weak Acids			
Acid	**Formula**	K_a **at 25 °C**	**Lewis Structure**
acetic	CH_3CO_2H	1.8×10^{-5}	
arsenic	H_3AsO_4	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	
	$HAsO_4^{2-}$	5.1×10^{-12}	

Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
arsenous	H_3AsO_3	5.1×10^{-10}	
boric	H_3BO_3	5.4×10^{-10}	
carbonic	H_2CO_3	4.3×10^{-7}	
	HCO_3^-	4.7×10^{-11}	

Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
cyanic	$HCNO$	2×10^{-4}	
formic	HCO_2H	1.8×10^{-4}	
hydrazoic	HN_3	2.5×10^{-5}	
hydrocyanic	HCN	4.9×10^{-10}	
hydrofluoric	HF	3.5×10^{-4}	
hydrogen peroxide	H_2O_2	2.4×10^{-12}	
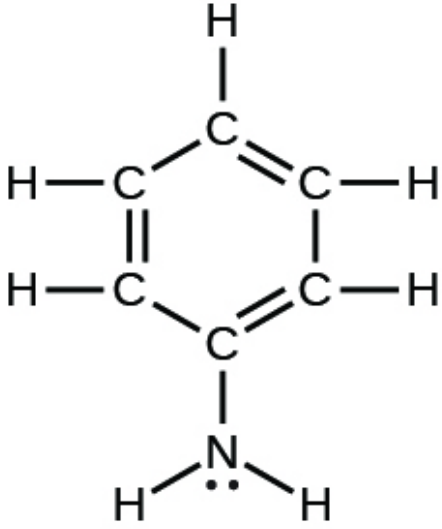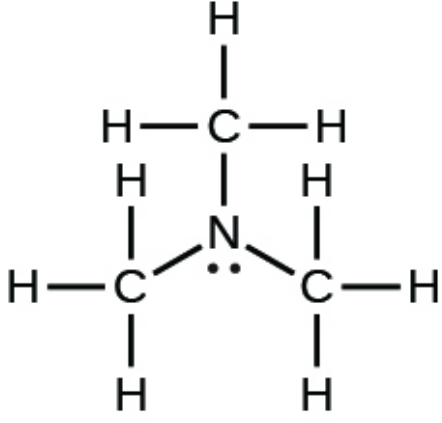
Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
hydrogen selenide	H_2Se	1.29×10^{-4}	
	HSe^-	1×10^{-12}	
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	

Ionization Constants of Weak Acids

Acid	Formula	K_a at 25 °C	Lewis Structure
	HTe^-	1.6×10^{-11}	
hypobromous	$HBrO$	2.8×10^{-9}	
hypochlorous	$HClO$	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	
oxalic	$H_2C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^-$	6.1×10^{-5}	
phosphoric	H_3PO_4	7.5×10^{-3}	

Ionization Constants of Weak Acids			
Acid	**Formula**	K_a at 25 °C	**Lewis Structure**
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

Ionization Constants of Weak Bases

Ionization Constants of Weak Bases		
Base	**Lewis Structure**	**K_b at 25 °C**
ammonia	$\begin{array}{c} \ddot{} \\ H\!-\!N\!-\!H \\ \mid \\ H \end{array}$	1.8×10^{-5}
dimethylamine	$\begin{array}{ccc} H & H & H \\ \mid & \mid & \mid \\ H\!-\!C\!-\!N\!-\!C\!-\!H \\ \mid & \ddot{} & \mid \\ H & & H \end{array}$	5.9×10^{-4}
methylamine	$\begin{array}{cc} H & \\ \mid & \ddot{} \\ H\!-\!C\!-\!N\!-\!H \\ \mid & \mid \\ H & H \end{array}$	4.4×10^{-4}

Ionization Constants of Weak Bases		
Base	**Lewis Structure**	K_b at 25 °C
phenylamine (aniline)		4.3×10^{-10}
trimethylamine		6.3×10^{-5}

Solubility Products

Solubility Products	
Substance	K_{sp} **at 25 °C**
aluminum	
$Al(OH)_3$	2×10^{-32}
barium	
$BaCO_3$	1.6×10^{-9}
$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}
$BaSO_4$	2.3×10^{-8}
$BaCrO_4$	8.5×10^{-11}
BaF_2	2.4×10^{-5}
$Ba(OH)_2 \cdot 8H_2O$	5.0×10^{-3}
$Ba_3(PO_4)_2$	6×10^{-39}
$Ba_3(AsO_4)_2$	1.1×10^{-13}
bismuth	
$BiO(OH)$	4×10^{-10}

Solubility Products

Substance	K_{sp} at 25 °C
BiOCl	1.8×10^{-31}
Bi_2S_3	1×10^{-97}
cadmium	
$Cd(OH)_2$	5.9×10^{-15}
CdS	1.0×10^{-28}
$CdCO_3$	5.2×10^{-12}
calcium	
$Ca(OH)_2$	1.3×10^{-6}
$CaCO_3$	8.7×10^{-9}
$CaSO4 \cdot 2H_2O$	6.1×10^{-5}
$CaC_2O_4 \cdot H_2O$	1.96×10^{-8}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$CaHPO_4$	7×10^{-7}
CaF_2	4.0×10^{-11}
chromium	
$Cr(OH)_3$	6.7×10^{-31}

Solubility Products

Substance	K_{sp} at 25 °C
cobalt	
$Co(OH)_2$	2.5×10^{-16}
$CoS(\alpha)$	5×10^{-22}
$CoS(\beta)$	3×10^{-26}
$CoCO_3$	1.4×10^{-13}
$Co(OH)_3$	2.5×10^{-43}
copper	
$CuCl$	1.2×10^{-6}
$CuBr$	6.27×10^{-9}
CuI	1.27×10^{-12}
$CuSCN$	1.6×10^{-11}
Cu_2S	2.5×10^{-48}
$Cu(OH)_2$	2.2×10^{-20}
CuS	8.5×10^{-45}
$CuCO_3$	2.5×10^{-10}
iron	

Solubility Products

Substance	K_{sp} at 25 °C
$Fe(OH)_2$	1.8×10^{-15}
$FeCO_3$	2.1×10^{-11}
FeS	3.7×10^{-19}
$Fe(OH)_3$	4×10^{-38}
lead	
$Pb(OH)_2$	1.2×10^{-15}
PbF_2	4×10^{-8}
$PbCl_2$	1.6×10^{-5}
$PbBr_2$	4.6×10^{-6}
PbI_2	1.4×10^{-8}
$PbCO_3$	1.5×10^{-15}
PbS	7×10^{-29}
$PbCrO_4$	2×10^{-16}
$PbSO_4$	1.3×10^{-8}
$Pb_3(PO_4)_2$	1×10^{-54}
magnesium	

Solubility Products	
Substance	K_{sp} **at 25 °C**
$Mg(OH)_2$	8.9×10^{-12}
$MgCO_3 \cdot 3H_2O$	*ca* 1×10^{-5}
$MgNH_4PO_4$	3×10^{-13}
MgF_2	6.4×10^{-9}
MgC_2O_4	7×10^{-7}
manganese	
$Mn(OH)_2$	2×10^{-13}
$MnCO_3$	8.8×10^{-11}
MnS	2.3×10^{-13}
mercury	
$Hg_2O \cdot H_2O$	3.6×10^{-26}
Hg_2Cl_2	1.1×10^{-18}
Hg_2Br_2	1.3×10^{-22}
Hg_2I_2	4.5×10^{-29}
Hg_2CO_3	9×10^{-15}
Hg_2SO_4	7.4×10^{-7}

Solubility Products

Substance	K_{sp} at 25 °C
Hg_2S	1.0×10^{-47}
Hg_2CrO_4	2×10^{-9}
HgS	1.6×10^{-54}
nickel	
$Ni(OH)_2$	1.6×10^{-16}
$NiCO_3$	1.4×10^{-7}
$NiS(\alpha)$	4×10^{-20}
$NiS(\beta)$	1.3×10^{-25}
potassium	
$KClO_4$	1.05×10^{-2}
K_2PtCl_6	7.48×10^{-6}
$KHC_4H_4O_6$	3×10^{-4}
silver	
$\frac{1}{2}Ag_2O(Ag^+ + OH^-)$	2×10^{-8}
$AgCl$	1.6×10^{-10}
$AgBr$	5.0×10^{-13}

Solubility Products

Substance	K_{sp} at 25 °C
AgI	1.5×10^{-16}
AgCN	1.2×10^{-16}
AgSCN	1.0×10^{-12}
Ag_2S	1.6×10^{-49}
Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	9.0×10^{-12}
$Ag_4Fe(CN)_6$	1.55×10^{-41}
Ag_2SO_4	1.2×10^{-5}
Ag_3PO_4	1.8×10^{-18}
strontium	
$Sr(OH)_2 \cdot 8H_2O$	3.2×10^{-4}
$SrCO_3$	7×10^{-10}
$SrCrO_4$	3.6×10^{-5}
$SrSO_4$	3.2×10^{-7}
$SrC_2O_4 \cdot H_2O$	4×10^{-7}
thallium	

Solubility Products

Substance	K_{sp} at 25 °C
TlCl	1.7×10^{-4}
TlSCN	1.6×10^{-4}
Tl_2S	6×10^{-22}
$Tl(OH)_3$	6.3×10^{-46}
tin	
$Sn(OH)_2$	3×10^{-27}
SnS	1×10^{-26}
$Sn(OH)_4$	1.0×10^{-57}
zinc	
$ZnCO_3$	2×10^{-10}

Standard Electrode (Half-Cell) Potentials

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	$E°$ **(V)**
$Ag^+ + e^- \longrightarrow Ag$	+0.7996
$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.22233
$[Ag(CN)_2]^- + e^- \longrightarrow Ag + 2CN^-$	−0.31
$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4{}^{2-}$	+0.45
$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3$	+0.373
$[Ag(S_2O_3)_2]^{3+} + e^- \longrightarrow Ag + 2S_2O_3{}^{2-}$	+0.017
$[AlF_6]^{3-} + 3e^- \longrightarrow Al + 6F^-$	−2.07
$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
$Am^{3+} + 3e^- \longrightarrow Am$	−2.048
$Au^{3+} + 3e^- \longrightarrow Au$	+1.498
$Au^+ + e^- \longrightarrow Au$	+1.692
$Ba^{2+} + 2e^- \longrightarrow Ba$	−2.912
$Be^{2+} + 2e^- \longrightarrow Be$	−1.847

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$Br_2(aq) + 2e^- \longrightarrow 2Br^-$	+1.0873
$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.868
$Ce^3 + 3e^- \longrightarrow Ce$	−2.483
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61
$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.4030
$[Cd(CN)_4]^{2-} + 2e^- \longrightarrow Cd + 4CN^-$	−1.09
$[Cd(NH_3)_4]^{2+} + 2e^- \longrightarrow Cd + 4NH_3$	−0.61
$CdS + 2e^- \longrightarrow Cd + S^{2-}$	−1.17
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.35827
$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$ClO_3^- + H_2O + 2e^- \longrightarrow ClO_2^- + 2OH^-$	+0.33
$ClO_2^- + H_2O + 2e^- \longrightarrow ClO^- + 2OH^-$	+0.66
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89
$ClO_4^- + 2H_3O^+ + 2e^- \longrightarrow ClO_3^- + 3H_2O$	+1.189
$ClO_3^- + 3H_3O^+ + 2e^- \longrightarrow HClO_2 + 4H_2O$	+1.21
$HClO + H_3O^+ + 2e^- \longrightarrow Cl^- + 2H_2O$	+1.482

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$HClO + H_3O^+ + e^- \longrightarrow \frac{1}{2}Cl_2 + 2H_2O$	+1.611
$HClO_2 + 2H_3O^+ + 2e^- \longrightarrow HClO + 3H_2O$	+1.628
$Co^{3+} + e^- \longrightarrow Co^{2+} \ (2 \ mol \ // \ H_2SO_4)$	+1.83
$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$[Co(NH_3)_6]^{3+} + e^- \longrightarrow [Co(NH_3)_6]^{2+}$	+0.1
$Co(OH)_3 + e^- \longrightarrow Co(OH)_2 + OH^-$	+0.17
$Cr^3 + 3e^- \longrightarrow Cr$	−0.744
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.407
$Cr^{2+} + 2e^- \longrightarrow Cr$	−0.913
$[Cu(CN)_2]^- + e^- \longrightarrow Cu + 2CN^-$	−0.43
$CrO_4{}^{2-} + 4H_2O + 3e^- \longrightarrow Cr(OH)_3 + 5OH^-$	−0.13
$Cr_2O_7{}^{2-} + 14H_3O^+ + 6e^- \longrightarrow 2Cr^{3+} + 21H_2O$	+1.232
$[Cr(OH)_4]^- + 3e^- \longrightarrow Cr + 4OH^-$	−1.2
$Cr(OH)_3 + 3e^- \longrightarrow Cr + 3OH^-$	−1.48
$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.153

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Cu^+ + e^- \longrightarrow Cu$	+0.521
$F_2 + 2e^- \longrightarrow 2F^-$	+2.866
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.447
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_2 + 2e^- \longrightarrow Fe + 2OH^-$	−0.88
$FeS + 2e^- \longrightarrow Fe + S^{2-}$	−1.01
$Ga^{3+} + 3e^- \longrightarrow Ga$	−0.549
$Gd^{3+} + 3e^- \longrightarrow Gd$	−2.279
$\frac{1}{2}H_2 + e^- \longrightarrow H^-$	−2.23
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	−0.8277
$H_2O_2 + 2H_3O^+ + 2e^- \longrightarrow 4H_2O$	+1.776
$2H_3O^+ + 2e^- \longrightarrow H_2 + 2H_2O$	0.00
$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^-$	+0.878
$Hf^{4+} + 4e^- \longrightarrow Hf$	−1.55

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.851
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.7973
$[HgBr_4]^{2-} + 2e^- \longrightarrow Hg + 4Br^-$	+0.21
$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.26808
$[Hg(CN)_4]^{2-} + 2e^- \longrightarrow Hg + 4CN^-$	−0.37
$[HgI_4]^{2-} + 2e^- \longrightarrow Hg + 4I^-$	−0.04
$HgS + 2e^- \longrightarrow Hg + S^{2-}$	−0.70
$I_2 + 2e^- \longrightarrow 2I^-$	+0.5355
$In^{3+} + 3e^- \longrightarrow In$	−0.3382
$K^+ + e^- \longrightarrow K$	−2.931
$La^{3+} + 3e^- \longrightarrow La$	−2.52
$Li^+ + e^- \longrightarrow Li$	−3.04
$Lu^{3+} + 3e^- \longrightarrow Lu$	−2.28
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.185

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$MnO_2 + 2H_2O + 2e^- \longrightarrow Mn(OH)_2 + 2OH^-$	−0.05
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.558
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.507
$Na^+ + e^- \longrightarrow Na$	−2.71
$Nd^{3+} + 3e^- \longrightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.257
$[Ni(NH_3)_6]^{2+} + 2e^- \longrightarrow Ni + 6NH_3$	−0.49
$NiO_2 + 4H^+ + 2e^- \longrightarrow Ni^{2+} + 2H_2O$	+1.593
$NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$	+0.49
$NiS + 2e^- \longrightarrow Ni + S^{2-}$	+0.76
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.957
$NO_3^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$	+0.92
$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^-$	+0.10
$Np^{3+} + 3e^- \longrightarrow Np$	−1.856
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.401

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	+0.695
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.1262
$PbO_2 + SO_4{}^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.69
$PbS + 2e^- \longrightarrow Pb + S^{2-}$	−0.95
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4{}^{2-}$	−0.3505
$Pd^{2+} + 2e^- \longrightarrow Pd$	+0.987
$[PdCl_4]^{2-} + 2e^- \longrightarrow Pd + 4Cl^-$	+0.591
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20
$[PtBr_4]^{2-} + 2e^- \longrightarrow Pt + 4Br^-$	+0.58
$[PtCl_4]^{2-} + 2e^- \longrightarrow Pt + 4Cl^-$	+0.755
$[PtCl_6]^{2-} + 2e^- \longrightarrow [PtCl_4]^{2-} + 2Cl^-$	+0.68
$Pu^3 + 3e^- \longrightarrow Pu$	−2.03
$Ra^{2+} + 2e^- \longrightarrow Ra$	−2.92
$Rb^+ + e^- \longrightarrow Rb$	−2.98
$[RhCl_6]^{3-} + 3e^- \longrightarrow Rh + 6Cl^-$	+0.44

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$S + 2e^- \longrightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \longrightarrow H_2S$	+0.142
$Sc^{3+} + 3e^- \longrightarrow Sc$	−2.09
$Se + 2H^+ + 2e^- \longrightarrow H_2Se$	−0.399
$[SiF_6]^{2-} + 4e^- \longrightarrow Si + 6F^-$	−1.2
$SiO_3{}^{2-} + 3H_2O + 4e^- \longrightarrow Si + 6OH^-$	−1.697
$SiO_2 + 4H^+ + 4e^- \longrightarrow Si + 2H_2O$	−0.86
$Sm^{3+} + 3e^- \longrightarrow Sm$	−2.304
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.151
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.1375
$[SnF_6]^{2-} + 4e^- \longrightarrow Sn + 6F^-$	−0.25
$SnS + 2e^- \longrightarrow Sn + S^{2-}$	−0.94
$Sr^{2+} + 2e^- \longrightarrow Sr$	−2.89
$TeO_2 + 4H^+ + 4e^- \longrightarrow Te + 2H_2O$	+0.593
$Th^{4+} + 4e^- \longrightarrow Th$	−1.90
$Ti^{2+} + 2e^- \longrightarrow Ti$	−1.630

Standard Electrode (Half-Cell) Potentials

Half-Reaction	$E°$ (V)
$U^{3+} + 3e^- \longrightarrow U$	−1.79
$V^{2+} + 2e^- \longrightarrow V$	−1.19
$Y^{3+} + 3e^- \longrightarrow Y$	−2.37
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.7618
$[Zn(CN)_4]^{2-} + 2e^- \longrightarrow Zn + 4CN^-$	−1.26
$[Zn(NH_3)_4]^{2+} + 2e^- \longrightarrow Zn + 4NH_3$	−1.04
$Zn(OH)_2 + 2e^- \longrightarrow Zn + 2OH^-$	−1.245
$[Zn(OH)_4]^2 + 2e^- \longrightarrow Zn + 4OH^-$	−1.199
$ZnS + 2e^- \longrightarrow Zn + S^{2-}$	−1.40
$Zr^4 + 4e^- \longrightarrow Zr$	−1.539

Half-Lives for Several Radioactive Isotopes

Isotope	Half-Life[footnote] y = years, d = days, h = hours, m = minutes, s = seconds	Type of Emission[footnote] *E.C.* = electron capture, *S.F.* = Spontaneous fission	Isotope	Half-Life[footnote] y = years, d = days, h = hours, m = minutes, s = seconds	Type of Emission[footnote] *E.C.* = electron capture, *S.F.* = Spontaneous fission
$^{14}_{6}\text{C}$	5730 y	(β^-)	$^{210}_{83}\text{Bi}$	5.01 d	(β^-)
$^{13}_{7}\text{N}$	9.97 m	(β^+)	$^{212}_{83}\text{Bi}$	60.55 m	$(\alpha \text{ or } \beta^-)$
$^{15}_{9}\text{F}$	4.1×10^{-22} s	(p)	$^{210}_{84}\text{Po}$	138.4 d	(α)
$^{24}_{11}\text{Na}$	15.00 h	(β^-)	$^{212}_{84}\text{Po}$	3×10^{-7} s	(α)
$^{32}_{15}\text{P}$	14.29 d	(β^-)	$^{216}_{84}\text{Po}$	0.15 s	(α)
$^{40}_{19}\text{K}$	1.27×10^{9} y	$(\beta \text{ or } E.C.)$	$^{218}_{84}\text{Po}$	3.05 m	(α)
$^{49}_{26}\text{Fe}$	0.08 s	(β^+)	$^{215}_{85}\text{At}$	1.0×10^{-4} s	(α)
$^{60}_{26}\text{Fe}$	2.6×10^{6} y	(β^-)	$^{218}_{85}\text{At}$	1.6 s	(α)
$^{60}_{27}\text{Co}$	5.27 y	(β^-)	$^{220}_{86}\text{Rn}$	55.6 s	(α)
$^{87}_{37}\text{Rb}$	4.7×10^{10} y	(β^-)	$^{222}_{86}\text{Rn}$	3.82 d	(α)
$^{90}_{38}\text{Sr}$	29 y	(β^-)	$^{224}_{88}\text{Ra}$	3.66 d	(α)
$^{115}_{49}\text{In}$	5.1×10^{15} y	(β^-)	$^{226}_{88}\text{Ra}$	1600 y	(α)
$^{131}_{53}\text{I}$	8.040 d	(β^-)	$^{228}_{88}\text{Ra}$	5.75 y	(β^-)
$^{142}_{58}\text{Ce}$	5×10^{15} y	(α)	$^{228}_{89}\text{Ac}$	6.13 h	(β^-)
$^{208}_{81}\text{Tl}$	3.07 m	(β^-)	$^{228}_{90}\text{Th}$	1.913 y	(α)
$^{210}_{82}\text{Pb}$	22.3 y	(β^-)	$^{232}_{90}\text{Th}$	1.4×10^{10} y	(α)
$^{212}_{82}\text{Pb}$	10.6 h	(β^-)	$^{233}_{90}\text{Th}$	22 m	(β^-)
$^{214}_{82}\text{Pb}$	26.8 m	(β^-)	$^{234}_{90}\text{Th}$	24.10 d	(β^-)

$^{206}_{83}\text{Bi}$	6.243 d	$(E.C.)$	$^{233}_{91}\text{Pa}$	27 d	(β^-)
$^{233}_{92}\text{U}$	1.59×10^5 y	(α)	$^{242}_{96}\text{Cm}$	162.8 d	(α)
$^{234}_{92}\text{U}$	2.45×10^5 y	(α)	$^{243}_{97}\text{Bk}$	4.5 h	$(\alpha \text{ or } E.C.)$
$^{235}_{92}\text{U}$	7.03×10^8 y	(α)	$^{253}_{99}\text{Es}$	20.47 d	(α)
$^{238}_{92}\text{U}$	4.47×10^9 y	(α)	$^{254}_{100}\text{Fm}$	3.24 h	$(\alpha \text{ or } S.F.)$
$^{239}_{92}\text{U}$	23.54 m	(β^-)	$^{255}_{100}\text{Fm}$	20.1 h	(α)
$^{239}_{93}\text{Np}$	2.3 d	(β^-)	$^{256}_{101}\text{Md}$	76 m	$(\alpha \text{ or } E.C.)$
$^{239}_{94}\text{Pu}$	2.407×10^4 y	(α)	$^{254}_{102}\text{No}$	55 s	(α)
$^{239}_{94}\text{Pu}$	6.54×10^3 y	(α)	$^{257}_{103}\text{Lr}$	0.65 s	(α)
$^{241}_{94}\text{Pu}$	14.4 y	$(\alpha \text{ or } \beta^-)$	$^{260}_{105}\text{Ha}$	1.5 s	$(\alpha \text{ or } S.F.)$
$^{241}_{95}\text{Am}$	432.2 y	(α)	$^{263}_{106}\text{Sg}$	0.8 s	$(\alpha \text{ or } S.F.)$